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REACTOR FUEL PROCESSING

A Quarterly Technical Progress Review

Prepared for U. S. ATOMIC ENERGY COMMISSION by ARGONNE NATIONAL LABORATORY



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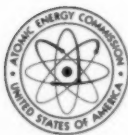
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A REVIEW OF RECENT DEVELOPMENTS

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foreword

This quarterly review of reactor fuel processing has been prepared at the request of the U. S. Atomic Energy Commission, Office of Technical Information. It is intended to assist those interested in keeping abreast of important developments in this field. In each Review it is planned to cover those particular subjects in which significant new results have been obtained. The Review does not purport to abstract all the literature published on this field during the quarter. Instead it is intended to bring each subject up to date from time to time as circumstances warrant.

Interpretation of results, where given, represents the opinion of the editors of the Review, who are personnel of the Argonne National Laboratory, Chemical Engineering Division. Those taking part in the preparation of this issue are J. Barghusen, L. Burris, Jr., A. A. Chilenskas, I. G. Dillon, P. Fineman, J. Fischer, A. A. Jonke, S. Lawroski, W. J. Mecham, J. Royal, W. B. Seefeldt, V. G. Trice, and R. C. Vogel. The reader is urged to consult the original references for more complete information on the subject reported and for the interpretation of results by the original authors.

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Section

I

COMMERCIAL ASPECTS OF FUEL PROCESSING

Recycle Value of Bred Reactor Fuel

The AEC buy-back prices for U^{233} and plutonium relative to U^{235} have been set by administrative action rather than by the supply and demand forces of a free market. In a recently published article an attempt has been made to estimate the relative value of these fissionable isotopes with respect to their use for recycle to power reactors.¹ The basis for the evaluation was to calculate a value for the bred fuel that would make the energy cost for the equilibrium fuel cycle (established by recycling the bred fuel) equal to the energy cost of the initial fuel cycle in which U^{235} is the fissionable isotope. In other words it was assumed that the market value of the bred fuel would be determined by competition with U^{235} . In comparing the value of the three fissionable isotopes, it was necessary to make allowances for the difference in the number of neutrons produced per fission and the difference in fuel fabrication costs. An attempt was made to estimate the increased cost of fabrication of fuels containing U^{233} or plutonium, arising from the extra precautions necessary in handling these materials, as compared with U^{235} . In connection with the possibility of recycling plutonium (produced in converter reactors) into fast breeder reactors, an attempt was made to evaluate the higher fabrication and processing costs arising from the much greater surface-to-mass ratio of fuel elements for fast breeders compared with thermal reactors.

The author concluded¹ that the AEC buy-back price for U^{233} relative to plutonium was too low. In thermal reactors, assuming that the fabrication costs of fuels containing U^{233} and plutonium are equal, the analysis indicates that U^{233} should be worth about \$12 per gram more than pluto-

nium (per gram of Pu^{239} and Pu^{241}). These conclusions were not altered by considering the value of plutonium in fast reactors. In the thermal converter-fast breeder cycle, the value of plutonium was estimated to be less than \$7 per gram.

The author suggests¹ that, "to minimize distortion and provide a maximum of encouragement to the development of economic nuclear power," a price of \$6 to \$8 per gram for plutonium and \$18 to \$20 per gram for U^{233} appears to be reasonable.

Fuel-Processing Plans

The Davison Chemical Division of W. R. Grace and Co., in cooperation with Bechtel Corp., has completed a report on the technical and economic feasibility of building a privately owned chemical processing plant for spent nuclear fuels. The report has been distributed to the five utility members of the Industrial Reprocessing Group, and a decision based on the report was expected to be reached during the fall of 1960. Meanwhile, the AEC has temporarily suspended its plans to expand its facilities for processing power-reactor fuels at Hanford, Idaho, Oak Ridge, and Savannah River.²

Construction of an auxiliary building was begun in July 1960 for the \$15 million Eurochemic (European Company for the Chemical Processing of Irradiated Fuels) project at Mol, Belgium. Construction of the research laboratory at Mol was scheduled to begin at the end of 1960, and construction of the plant itself is scheduled to begin in the summer of 1961. Operation is expected to begin in 1964. Eurochemic is financed by 13 European nations. Approximately 20 per cent of the capital stock (\$21.5 million) is held by private organizations, the remainder being

owned by the governments and other public bodies of the 13 nations.² The USAEC has provided assistance to Eurochemic in the form of several full-time or part-time consultants and personnel for the review and exchange of technical data pertinent to the processing of irradiated fuels.³

France plans to construct a second plutonium separation plant, at Jobourg, to process irradiated fuel elements from power reactors now under construction or planned for northwestern France. The capacity of the plant has not been officially announced but is believed to be somewhat less than that of the chemical separation plant operating at Marcoule since 1958. Construction is tentatively scheduled to start⁴ early in 1961.

South Africa's first uranium refining plant, with a capacity of 100 tons of uranium per year, is ready to go into operation at Johannesburg. The plant will enable South Africa to do its own research on uranium processing techniques as well as to refine part of its own output. Contracts with the United States and Great Britain for uranium concentrates totaling over 6200 tons per year will begin to run out in about 18 months and have not been extended. It is believed that the refining plant will place the country in a more favorable position to offer uranium in a competitive world market.⁴

Transport of Fuel Materials

The Bureau of Explosives, an advisory group to the Interstate Commerce Commission (ICC), has suggested the formation of an AEC-industry committee to study and make recommendations on the safe transport of fissionable materials. The committee is to consider fabricated and unfabricated materials, both irradiated and non-irradiated. The Bureau's proposal was explored at a meeting in August 1960 with representatives of the AEC and its contractors. At the meeting a small committee was organized to work out details and make recommendations.⁴

One aspect of this problem, the shipment of radioactive fuel elements from the reactor operator to the processing site, is under study at Oak Ridge National Laboratory (ORNL). Spent fuel-element carriers must be designed to give adequate radiation shielding, to contain radioactivity under accident conditions, and to conform with governmental regulations. In addition

to conforming to these restrictions, the method of shipment must be economically feasible. Criticality and shielding problems have been studied, but they do not appear to present the difficulties that heat dissipation (from radioactive decay) does. It is assumed in design studies that the fuel elements and carrier construction materials should not be allowed to approach closer than 100°C to their melting points in the absence of internal coolants. Because of the low melting point of lead, it may be necessary to consider steel, iron, or uranium for shielding material. The study indicates that heat generation in the fuel element may severely restrict the number of elements per carrier and/or require long cooling periods before shipment.⁵

Enriched-Uranium Production

Considerable interest has developed in the last two years in the re-emergence of gas ultracentrifuging as a promising means for enriching uranium. Many groups, both foreign and domestic, have exploited high-tensile-strength materials not available 15 years ago to develop small, high-speed centrifuges which offer the real possibility—although not as yet the assurance—of producing fissionable material at reasonable cost. U. S. firms interested in gas centrifuging include Thor-Westcliffe, Decker Corp., General Electric, Mallinckrodt, and Sharples Corp.

An economic appraisal of gas centrifuging has been attempted in a report, prepared under AEC contract, by Zippe, a West German scientist who was recently awarded a German patent on gas centrifuges.⁶ Extrapolating cost data to a small German Degussa machine of recent design, the cost of separating U²³⁵ was estimated at \$301 per kilogram per year, as compared with \$135 per kilogram per year for gaseous diffusion. The uncertainty in the calculation is the cost of the auxiliary equipment in a cascade arrangement. A larger Degussa machine is under development. The author believes that, if larger and faster centrifuge machines are used, the cost of separation might very well compete with gaseous diffusion.

Uranium Procurement

AEC uranium procurement costs for the total fiscal year 1961 will be about 10 per cent less

than 1960 costs. The reduction in expenditure is largely due to the effort made to defer to the 1962-1966 period a portion of the deliveries under domestic and foreign contracts which otherwise would have been delivered earlier. The average price per pound of U_3O_8 in the fiscal year 1961 is estimated at \$9.76 as compared to a cost of \$10.12 in 1960. Of the anticipated 32,000 tons to be received in the fiscal year 1961, 55 per cent will come from domestic suppliers, 32 per cent from Canada, and 13 per cent from overseas sources. The last of deliveries under the Belgian Congo agreement were received in September 1960. Deliveries from Portugal and Australia will be completed in calendar year 1962. Procurement⁷ from South Africa will continue through 1966.

Radioisotope Production

To encourage development of ionizing radiation as a major industrial processing tool, the AEC has lowered its price for Co^{60} to \$1 per curie for material with a specific activity below 55 curies per gram in quantities greater than 100,000 curies. For smaller amounts the new price is dependent on the specific activity: 1 to 25 curies per gram, \$2 per curie; 25 to 40 curies per gram, \$3 per curie; 40 to 55 curies per gram, \$4 per curie. These quantity discounts were established: 25 per cent for quantities of 5001 to 25,000 curies; 50 per cent for 25,001 to 100,000 curies.⁸

Consideration is being given to construction of the first private fission-product radioisotope separations facility in the world by the Martin Company and the Air Reduction Company, which would form a new company to build and operate it. The new company would produce Sr^{90} , Cs^{137} , and possibly Ce^{144} , with the AEC furnishing the feed material and buying back most or all of the separated isotopic material. Martin has estimated that a large plant could produce Sr^{90} for 35 to 50 cents per curie, or one-tenth of the AEC price. Arrangements would have to be made for locating the plant on AEC-owned land. Hanford or a site near Hanford is the preferred location.

The Multicurie Fission-Product Pilot Plant at ORNL has been modified during a nine-month shutdown to provide increased capacity and permit simultaneous separation of five products: Cs^{137} , Sr^{90} , Pm^{147} , Ce^{144} , and Tc^{99} . Even when in

full operation, however, the pilot plant will not be able to meet the demand for some isotopes, particularly Sr^{90} and Cs^{137} . An unusually heavy demand has developed for substantial quantities of radioisotopes primarily for isotopic-powered generators.⁹

Abbott Laboratories began marketing I^{131} in September 1960, and Abbott is expected eventually to supply a major share of the estimated 100 curies per month used by itself and others in the United States. The I^{131} is to be produced from Te^{130} in the Westinghouse Testing Reactor and is to be marketed in sodium radioiodide solution by Abbott's Oak Ridge plant.⁴

Waste-Disposal Licensing

The AEC's procedure for licensing industrial waste-disposal firms is facing a federal court test. Harris County, Tex., has petitioned the U. S. Court of Appeals, Fifth Circuit, for review of an AEC order issuing a by-product (radioisotope) material license to the Industrial Waste Disposal Corp. of Houston, Tex. The license, issued in August, authorized the company to receive and store limited amounts of waste material destined for disposal by land burial at the AEC's Oak Ridge or Idaho sites. In its petition for review of the decision, Harris County alleges that the Atomic Energy Act does not provide authority to license possession of by-product material for disposal, and that there was "collusion" between the AEC and the company. The AEC said that it presumed the charge stemmed from the customary statement of the AEC staff position, which was filed with the hearing examiner before the hearing, and pointed out that this has no binding effect on the hearing examiner or on the Commission itself.¹⁰

The AEC has issued¹⁰ a list of companies holding licenses to receive and dispose of radioactive wastes; this list is given in Table I-1.*

The AEC has given notice of intent to issue a license to Nuclear-Chem Disposal Corporation of Long Island, N. Y., to receive and store limited amounts of low-level radioactive waste and to transfer this material to Oak Ridge for land burial. Possession of radioactive material

*Table I-1 is adapted¹⁰ from *The Forum Memo to Members*, Atomic Industrial Forum, Inc.

Table I-1 COMPANIES LICENSED TO RECEIVE AND DISPOSE OF RADIOACTIVE WASTES¹⁰

Institution	Type of material authorized	Possession limit	Disposal sites*
Crossroads Marine Disposal Corp., Boston, Mass.	By-product	1000 curies	Atlantic Ocean; ORNL or Idaho Falls land sites
	Source	16,000 lb	
	Special nuclear	100 g	
California Salvage Co., San Pedro, Calif.	By-product	2 curies	Pacific Ocean
	Source	500 lb	
	Special nuclear	10 g	
American Mail Line, Ltd., Seattle, Wash.	By-product	10 curies	At sea, where depth exceeds 1000 fathoms
	Source	15 lb	
Walker Trucking Co., New Britain, Conn.	By-product	50 curies	Atlantic Ocean
	Source	700 lb	
Isotopes Specialties Div. of Nuclear Corp. of America	By-product	100 curies	Pacific Ocean
	Source	2000 lb	
	Special nuclear	20 g	
New England Tank Cleaning Co., Cambridge, Mass.	By-product	1000 curies	Atlantic Ocean
	Source	50 lb	
	Special nuclear	5 g	
Nuclear Engineering Co., Pleasanton, Calif. (or Naval Industrial Reserve Shipyard, Kearny, N. J.)	By-product	800 curies	Pacific Ocean
	Source	25,000 lb	
	Special nuclear	900 g	
Ocean Transport Co., San Francisco, Calif.	By-product	1000 curies	Pacific Ocean; ORNL or Idaho Falls land sites
	Source	4000 lb	
	Special nuclear	300 g	
Industrial Waste Disposal Corp., Houston, Tex.	By-product	10 curies	ORNL or Idaho Falls land sites
Radiological Services Co., Inc., Valley Stream, L. I., N. Y.	By-product	200 curies of atomic Nos. 3 and 83; 5 mc of Po ²¹⁰	ORNL or Idaho Falls land sites
	Source	2500 lb	
	Special nuclear	200 g	

*Specific locations of the ocean sites are given in reference 10.

would be limited to not more than 1000 curies of tritium, 100 curies of other by-product material, and 1000 lb of source material at any one time.¹¹

Nuclear Engineering Company of Pleasanton, Calif., recently objected to AEC's designation of the Idaho and Oak Ridge sites for land burial of radioactive wastes, contending that this placed the AEC in competition with commercial firms involved in disposal of wastes at sea. The company also submitted a proposal to the AEC for the selection, management, and operation of land disposal sites in California. The AEC responded that the need for long-term precautions indicated that responsibility should rest in a government entity. The AEC noted that the services of private waste-disposal concerns would be needed for land disposal at govern-

ment sites, just as they are needed for sea disposal.²

The AEC has issued for public comment a proposed regulatory amendment which would establish design and packing criteria for containers used in sea disposal of low-level radioactive waste material. The proposed criteria require that containers maintain their integrity until they reach at least 1000 fathoms (6000 ft), the disposal level required by Commission regulations. Commission standards for sea disposal are based on the fact that the ocean water will safely dilute and disperse the low-level wastes that are permitted to be disposed of at sea. The proposed amendment also provides for authorization for disposal at sea of waste radioactive metal without a disposal container, where it is shown that the metal will sink to 1000 fathoms.¹²

The AEC will test an underwater television camera in Massachusetts Bay, 15 miles off Boston Harbor, in making observations of a site formerly used for the disposal of low-level packaged radioactive wastes. A remote-controlled underwater vehicle will be used in the survey.¹³

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11. AEC to Issue Waste Disposal License to New York Firm, AEC Press Release C-170, Aug. 30, 1960.
12. AEC Issues Proposed Design Criteria for Sea Disposal Containers, AEC Press Release C-146, Aug. 15, 1960.
13. AEC to Test Underwater Television in Observing Waste Disposal, AEC Press Release C-139, July 20, 1960.

Section

II

SAFETY IN CHEMICAL PROCESSING

In a previous Review¹ a description was given of the explosion which occurred in a cell of the Hot Pilot Plant at ORNL on Nov. 20, 1959. Some additional details of this incident have been published.² It is stated that the explosion was due to the deflagration of nitrated organic compounds in an intercycle evaporator and involved nitration, by concentrated nitric acid, of 14 liters of the proprietary decontaminating agent, Turco 4501. Approximately 15 g of plutonium was released from the subcell that contained the evaporator; about 70 mg was released from cells 6 and 7 to the interior of Building 3019, and about 600 mg was released through the cell 7 door and deposited on nearby streets and building surfaces.

Building 3019 was not designed to contain the plutonium that was released from the evaporator by the explosion. The cell ventilation filters retained the alpha activity with a high degree of efficiency, but the existence of the cell 6 door, which opened readily, precluded confinement of the plutonium to Building 3019.

The decontamination of the interior of Building 3019, exclusive of processing cells 4 through 7, was 90 per cent complete on Aug. 1, 1960. Cleanup effort in cells 6 and 7 was started in April 1960 but was suspended pending installation of a temporary secondary-containment structure and provision of additional vessel off-gas capacity. These were not considered necessary at first because, although material balances had shown 4.6 ± 3.3 kg of plutonium missing, it was thought that no plutonium would be in the evaporator because of the series of decontamination treatments to which it had been subjected. However, flushing of the evaporator with water and nitric acid removed 109 g of plutonium. Cell cleanup will be resumed as soon as the new radiation safety requirements are met. Further information pertinent to the incident are covered

in several ORNL reports in preparation or completed.³⁻⁶

The results of a study of a radiation incident at ORNL in April 1959 have been released by the AEC. Eight persons in the Solid States Building received radiation exposure when an irradiated graphite-clad fuel element was being sawed in a hot cell and radioactive particles were carried out of the cell into the work area by a change in the air flow.⁷ Highest internal exposure of personnel was about 2 rems; all were well under maximum permissible annual dosage figures. Cleanup operations expected to cost \$39,500 were complicated by contamination of the ventilating system.⁸

Eight men involved in the criticality accident at the Y-12 Plant (Oak Ridge) in June 1958 have brought suit against the U. S. Government for a total of nearly \$1 million, claiming impaired eyesight, general weakening, stiffening of the joints, sterility, insomnia, and other ill effects of the accident. The eight men received varying degrees of exposure estimated by the AEC at a low of 20 rads ranging to a high of 320 rads.⁹ All returned to work shortly after the accident and are still employed at Oak Ridge.⁸

In a report submitted to the Congressional Joint Committee on Atomic Energy, the AEC outlined the studies and corrective work it is doing in the field of health and safety in uranium mills. Preliminary studies at Los Alamos suggest that the dust problem in mines may not be as serious as surveys have indicated, since the dust particle size is too large to permit inhalation to the lower lung, where the greatest physiological damage is caused. At AEC's Winchester (Mass.) Laboratory, studies on radioactive liquid effluents from mills have resulted in the development of chemical treatment processes which significantly reduce radioactive concentrations.¹⁰ These processes have already

been put into use. AEC said it had issued 23 notices of violations at various mills, and 11 orders have been issued requiring correction of deficiencies when followup inspections showed that appropriate action was not taken. The AEC has not taken action to stop operation of any mill because the data do not indicate an immediate hazard to public health and safety. The AEC has required the mills to initiate comprehensive programs of environmental sampling and radiochemical analysis to identify problem areas.⁸

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Section

III

PREPARATION FOR FUEL PROCESSING

A scheme for processing fuel elements from power reactors is described in a Hanford Atomic Products Operation (HAPO) report.¹ Current plans call for receiving and storage, mechanical treatment, dissolution, clarification, and solution storage at the Uranium Recovery Plant. Dissolver solution will be pumped to the Redox solvent-extraction plant for separation and decontamination of the uranium and plutonium. The decontaminated uranium product will be shipped as uranium nitrate solution to another AEC site for calcination.

A number of "head-end" processes are being considered in order to prepare, from the wide variety of nuclear reactor fuels, fuel solutions which are compatible with existing processing plants. Some head-end processes remove the cladding separately; some put cladding and fuel into a single solution. Mechanical decladding, chemical dejacketing, dissolution, and precipitation are discussed in this review.

Mechanical Processing

Many claddings for nuclear fuels are chemically resistant, and the fuels are of complex geometry. Therefore, for many of the proposed fuels, it would be desirable to remove the cladding material mechanically. Mechanical processing offers the important advantages of smaller aqueous waste volumes, the use of less corrosive reagents for dissolving the fuel material when the difficult-to-dissolve cladding is removed, and increased plant capacity in the absence of dissolved cladding material in process streams.

Three HAPO reports²⁻⁴ discuss mechanical processing aspects. Kelly² has investigated the size reduction of fuel elements by shearing, using a 40-ton HAPO-designed hydraulic shear.

The studies show² that a shear of 200- to 350-ton capacity will be required to shear the largest present-day fuels, with size dependent largely on blade geometry and velocity. For the shear, conventional silicon-manganese tool-steel blades will permit cutting in excess of 10 tons (uranium weight) of fuels per blade. During shearing, short fuel pieces (1 in. or greater in length) can be produced with cladding open at the ends. This allows acid-leaching of fuel core material. Significant quantities of dust, including submicron particles, will also be produced in shearing, particularly for oxide fuel. Dust containment studies are continuing for control and collection of shear dust.

Operation of the HAPO-designed 40-ton hydraulic shear equipped with a male V moving blade and semicircular stationary blade was continued, primarily to study life under varying conditions.⁵ Basically, the studies have shown little difference in the "wear rate" of shear blades operated at high and low velocities (50 to 70 in./sec blade velocity and 0.5 in./sec blade velocity). However, the greater effective capacity of the high-velocity shear, as compared to the low-velocity shear, was confirmed. Variations of blade life with material of manufacture are discussed.

Hammond and Kelly³ have studied removal of the hardware (including end fittings) from fuels assigned for HAPO processing. Hardware can be removed by hack sawing, cold sawing (slow-speed circular sawing), or high-speed circular sawing. With adequate clamping, hack sawing was considered the most desirable method. The evaluation of three types of hack saws employing different blade feed mechanisms was discussed in previous Reviews.^{6,7} With proper modification, it would be feasible to use any one of the saws tested for remote cell operation.³

The fuel elements of the Yankee power reactor (Rowe, Mass.) are currently scheduled for processing at HAPO. As received, the cross section of the Yankee fuel element is too large to fit into the critically safe dissolvers proposed for the processing of nonproduction fuels (NPF) at HAPO. The element will be reduced to nine full-length subassemblies. Then a suitable number of subassemblies will be used for each dissolver charging. The subassemblies are held together by end fittings and tie bands. The removal of end fittings is discussed above. Hammond and Kelly⁴ discuss various methods of band removal and disassembly. Use of slitting knives of various blade geometries to cut bands successfully was reported in a previous Review.⁷ This method was considered the best method for reducing Yankee fuel elements to subassemblies.

Studies on methods of safely handling NaK-containing fuel elements in the HAPO NPF mechanical cell are currently being completed.⁵ In recent hacksaw tests, steel capsules containing uranium-molybdenum alloy and reservoirs containing 8 g of NaK were successfully deactivated in a shallow pool of water covered by an inert-gas blanket. The uranium-molybdenum fuel did not ignite or react noticeably when the NaK reacted violently with the bath water. The tests to date indicate that up to 30 g of NaK (the maximum to be released during hacksaw operation) could be instantaneously released in the cell-hood system safely. A vigorous reaction occurs, but the equipment can easily be designed to withstand and dissipate the reaction energy.

Experimental tests on the shearing of stainless-steel-clad uranium dioxide fuel bundles both by ORNL and by two subcontractors were completed.⁸ The tests indicated the feasibility of the shear-and-leach approach to mechanical processing of fuel, and a 250-ton shear for hot-cell use was designed and is now being fabricated.

The Sodium Reactor Experiment (SRE) de-jacketing equipment at ORNL⁹ was satisfactorily operated by remote control in cold runs. A substitute high-viscosity fire-resistant hydraulic fluid (viscosity 225 Saybolt-sec Universal at 100°F) was successfully used in the hydraulically operated multipurpose saw.

Chemical De-jacketing

Selective chemical dissolution of fuel jackets and structural components is an attractive al-

ternate to mechanical de-jacketing or complete dissolution. The fuel cores thus exposed can be dissolved by another reagent in a second step. The principal materials used for cladding are aluminum, zirconium or Zircaloy, and stainless steel.

Removal of Zirconium and Zircaloy Jackets

Zirconium-clad or Zircaloy-clad fuel elements having oxide cores, such as Dresden or pressurized-water reactor (PWR) fuels, may be de-jacketed by the Zirflex process. In this process the cladding is dissolved in 6M ammonium fluoride-1M ammonium nitrate.

Development work at HAPO on the Zirflex process as applied to nonproduction fuels has now been completed,¹⁰ and HW-65979, The Zirflex Process Terminal Development Report, is being issued.

In studies at ORNL⁸ the Zirflex process for decladding PWR blanket elements (uranium dioxide pellets clad in Zircaloy-2) was demonstrated with fuel irradiated up to 1750 Mwd/ton. Uranium and plutonium losses to the 6M ammonium fluoride-1M ammonium nitrate decladding solution increased with increasing burnup. However, losses at maximum burnup were only 0.04 per cent uranium and 0.08 per cent plutonium. Data quoted in previous Reviews indicated that ammonia generated by the decladding reaction must be removed from the system to avoid formation of a zirconium dioxide-water sludge.^{7,11}

In engineering-scale development work at ORNL¹² on the Zirflex process for decladding Zircaloy-2-clad fuels, solutions which were stable at room temperature and which contained ~0.8M zirconium were produced by dissolution of Zircaloy-2 in 4.5M ammonium fluoride-0.5M ammonium nitrate. The average dissolution rate was acceptable, ~2 mg/(min)(sq in.).

Experiments are in progress at HAPO to determine the extent of attack by Zirflex decladding solutions on Plutonium Recycle Test Reactor (PRTR) spike fuel alloys.^{5,13} Alloys containing aluminum-plutonium-nickel and aluminum-plutonium-nickel-silicon were exposed for about 11 hr in decladding solutions (initial decladding solution: 2M ammonium fluoride-0.17M ammonium nitrate) while Zircaloy-2 was being dissolved and for 5 to 6 hr in the terminal decladding solution. Total penetration of the aluminum-plutonium-nickel

alloy was about 8 mils. This represents the removal of about 6 per cent from a $\frac{1}{2}$ -in.-diameter rod. Roughly two-thirds of the penetration occurred during the 6 hr when zirconium was not dissolving. Comparative penetration rates were not available. Maximum plutonium losses observed (calculated on the basis of radial penetration of the cores) were 2 to 3 per cent for a 2 per cent nickel-aluminum-plutonium-silicon alloy exposed to a decladding solution initially 2M ammonium fluoride-0.17M ammonium nitrate. Plutonium losses were somewhat lower for a 1 per cent nickel-1 per cent silicon-aluminum-plutonium alloy under the same conditions and for both alloys when exposed to a decladding solution initially 6M ammonium fluoride-0.5M ammonium nitrate.

A study of Zircaloy-2 dissolution rates in Zirflex decladding solutions as a function of pH and "free-fluoride" concentration has been completed.⁵ Data obtained permit the construction of a family of curves showing dependence of dissolution rate on pH for different solution compositions that might occur during the Zirflex decladding process. Ranges of pH covered (as measured in boiling solutions) were from 6 to about 7.5. Dissolution-rate dependence on hydrogen-ion concentration was the same for each of the solution compositions studied. Data indicate that the dissolution rate was proportional to $(H^+)^{0.5}$.

Further laboratory-scale experiments were made at HAPO to compare uranium losses to Zirflex decladding solutions for steam- and air-sparg removal of ammonia.⁵ Small Zircaloy-2-clad uranium dioxide fuel pieces, with and without oxide coating on the Zircaloy, were declad with 5.5M ammonium fluoride-0.5M ammonium nitrate. Terminal decladding solutions were diluted to 0.6M zirconium, cooled to room temperature, and allowed to stand without sparging for 24 hr. Uranium remaining in solution represented about 0.13 per cent loss (plant scale) when steam sparging was used for ammonia removal during decladding and about 0.35 per cent loss with air sparging during decladding.

Rates of attack of Zirflex decladding solutions on uranium-2 per cent zirconium alloy were determined for initial, midpoint, and terminal solutions.^{5,10} The tests were made in the absence of dissolving Zircaloy; consequently the pH values were low. Attack on the 2 per cent zirconium alloy was high, ranging from 2 g/(hr) (cm^2) in the initial solution to about 0.3 g/(hr)

(cm^2) in the terminal solution. These are all instantaneous rates based on short (2 min) exposures. The possibility of an induction period was not discussed. It is expected that the average rates for longer exposures would be less because of precipitation of U(IV) fluoride on the surface of the test piece.

Laboratory work at HAPO on decladding of Zircaloy-clad uranium dioxide fuels in acidic fluoride solutions has been concluded.¹⁰ A feasible decladding scheme was established. Corrosion tests indicate that one of the experimental alloys produced at Battelle Memorial Institute (BMI) (No. 20)* would be a satisfactory construction material. A report covering the work on this procedure is in preparation.

At Savannah River, electrolytic dissolution of zirconium in nitric acid is being investigated as an alternate to chemical decladding.¹⁴ In laboratory tests, only 15 per cent of the zirconium metal electrolytically disintegrated in nitric acid remained in solutions as ZrO^{++} . The remainder precipitated as zirconium dioxide. The split between soluble and insoluble species was insensitive to a fourfold change in acid concentration (4M to 16M) and a threefold change in current density (0.13 to 0.41 amp/ cm^2).

Electrolytic disintegration of zirconium-10 per cent uranium alloy effected the solution of 22 to 40 per cent of the zirconium, the remainder precipitating as zirconium dioxide. The loss of uranium to the precipitate was greater than 10 per cent in all tests. The loss decreased with increasing concentration of acid, but no definite correlation of loss with temperature was observed.

Removal of Stainless-Steel Jackets

Sulfex and Darex flow sheets for decladding Consolidated Edison Thorium Reactor (CETR) fuel elements were presented in an earlier Review.⁷ The Sulfex process involves dissolution of the cladding in an excess of ~6M sulfuric acid. The Darex process uses dilute aqua regia for decladding (5M nitric acid-2M hydrochloric acid). After decladding by either the Sulfex or Darex process, the core is dissolved in a solution of 13M nitric acid-0.04M sodium fluoride-0.04M aluminum nitrate.

*Composition, wt. %: nickel, 50; chromium, 25; molybdenum, 6; copper, 1; and iron, 16.

At ORNL the development of the Sulfex and Darex processes for decladding CETR fuel (stainless-steel-clad thorium dioxide-uranium dioxide pellets) was continued.⁸ Laboratory studies show that the 20-mil-thick stainless-steel cladding dissolved in the Darex reagent, boiling 5M nitric acid-2M hydrochloric acid, in 1 hr; the off-gas was a mixture of nitrogen oxides and nitrosyl chloride containing less than 0.5 vol.% hydrogen. Losses from intact and partly fragmented pellets were generally 0.05 to 0.5 per cent for uranium and 0.03 to 0.9 per cent for thorium; losses from highly fragmented pellets were as high as 9 per cent for uranium and 10 per cent for thorium.

In the Sulfex decladding process for CETR fuel, the stainless-steel cladding dissolved in 1 to 3 hr in 200 per cent excess of boiling 4M to 6M sulfuric acid; the off-gas is hydrogen.⁸ Uranium and thorium losses were slightly lower than in the Darex process. From unfragmented prototype fuel (pellets having 80 to 85 per cent of the theoretical density and irradiated from 0 to 445 Mw/ton), uranium and thorium losses varied randomly from 0.07 to 0.44 per cent and 0.04 to 0.33 per cent, respectively. When the fuel pellets shattered, uranium losses were as high as 1.8 per cent.

Fragmentation of the fuel pellets during irradiation not only could lead to higher decladding losses but also could result in the formation of slurries of fine core material, which would constitute a criticality hazard. Irradiation of thorium dioxide-uranium dioxide pellets by other workers has led to fragmentation in some cases but not in others. Accordingly, experiments were performed at ORNL¹⁵ to determine the power density (Mw/ton) required to crack 0.26-in.-diameter, 0.5-in.-long, 95 per cent thorium dioxide-uranium oxide pellets (93 per cent of theoretical density) which are similar to those which will be used in the first CETR core. Cracking was assumed to be due to the thermal gradient within a fuel element. It is assumed that the thermal gradient within a fuel element is established almost immediately after its insertion into a reactor. The pellets were irradiated only 3 min in the Oak Ridge Research Reactor (ORR) at power densities ranging from 16 to 160 Mw per metric ton of thorium. No fragmentation or cracking of the pellets occurred at these low irradiation levels. Variations in the irradiation conditions (16 to 160 Mw/ton) had no effect on the rate of disso-

lution of the pellets in boiling 13M nitric acid-0.04M sodium fluoride-0.1M aluminum nitrate.

Seven Sulfex decladdings of sintered uranium dioxide cores clad in type 304L stainless steel and two Sulfex partial dissolutions of stainless-steel pipe were performed in the recirculating dissolver pilot-scale facility at HAPO⁵ to determine the effect of substituting steam for air as the sparge gas. Sparging has been used as a means of agitation. In every case where steam was substituted for air as a sparge gas, a marked increase in reaction rate was observed, as indicated by the hydrogen evolution rates. As a consequence, the acid concentrations or reaction times necessary to effect rapid and complete decladdings can be reduced whenever steam is used in place of air. This also results in lowered uranium losses (0.03 per cent versus 0.07 per cent) and reduced corrosion of the Hastelloy F dissolver vessel (about 0.5 lb versus 1.5 lb of metal removed per decladding run).

The use of boron as a soluble neutron poison during Sulfex decladding has been reported in an earlier Review.⁷ Further investigations of soluble neutron poisons are being made at ORNL^{9,16} and HAPO.¹ Although soluble nuclear poisons have been suggested as reactor controls and as a safety measure in the processing of slightly enriched uranium, the difficulty of ensuring that the poisons remain in solution has been a deterrent in their use as a principal control of criticality in the processing of reactor fuels. If accepted as a means of criticality control, a complete study of the chemical behavior of the poisons will be made for specific flow sheets and conditions.

Laboratory experiments at ORNL^{9,16} demonstrated the apparent chemical feasibility of incorporating boron, cadmium, or rare-earth salts as nuclear poisons for criticality control during the processing of CETR fuel. At room temperature, up to 18 g of boric acid dissolved per liter of cladding or core dissolver solutions, i.e., 0.3M boric acid in decladding solution (6M sulfuric acid) and 0.3M boric acid in the dissolution reagent used in the Thorex flow sheet (13M nitric acid-0.04M fluoride-0.1M aluminum nitrate). Boric acid had no apparent effect on the dissolution of the stainless-steel jacket or thorium dioxide-uranium dioxide core. At room temperature the cadmium solubility in 5M sulfuric acid was 0.3M and was 1M in the 13M nitric acid solution used in the Thorex flow sheet. Gadolinium-samarium mixtures dis-

solved at concentrations up to 5 g/liter without difficulty. None of these neutron poisons were volatilized to a significant extent (i.e., they were <6 per cent volatilized) during evaporation for feed adjustment.

Dissolution

Of the chemical processes discussed here, some are designed for simultaneous dissolution of the jacket and core and others are designed for dissolution of de jacketed material. Processes for simultaneous dissolution of jacket and core are discussed for zirconium alloy, stainless-steel alloy, aluminum-plutonium alloy, and uranium alloy fuels. For zirconium alloy fuels, the dissolution processes being investigated include nitric acid-hydrofluoric acid dissolution, a modified Zirflex process, and the Alloy Reguline Chloride Oxidation (ARCO) (fused lead chloride) process. For stainless-steel alloy fuels, the proposed schemes include Darex and electrolytic dissolution in nitric acid. For aluminum-plutonium-silicon-nickel alloy fuels, mercuric nitrate-nitric acid dissolution is proposed. Processes for dissolution of de jacketed material are discussed for uranium-molybdenum alloy fuels and uranium carbide fuels. For uranium-molybdenum alloy fuels, a 12M to 14M nitric acid-ferric nitrate dissolution solution is proposed. Uranium carbide fuels may be dissolved in 90 per cent nitric acid.

Simultaneous Dissolution of Jacket and Core

Dissolution of Zirconium Fuel Elements in Nitric Acid-Hydrofluoric Acid Mixtures. Studies are being made at the Idaho Chemical Processing Plant (ICPP) to improve the nitric acid-hydrofluoric acid dissolution process for low uranium-zirconium alloys.¹⁷ An investigation of the mechanism of the dissolution of zirconium in solutions 2M to 13M nitric acid and 0.03M to 1.0M hydrofluoric acid led to the following conclusions:

1. The initial rate of dissolution of both zirconium and Zircaloy-2 at reflux temperatures exhibits a first-order dependency on the hydrofluoric acid concentration in nitric-hydrofluoric acid mixtures.

2. In these acid mixtures the nitric acid concentration has little effect on the initial zirconium dissolution rate, other than changing the

reflux temperature; the effect is more pronounced in the case of Zircaloy-2.

3. The activation energy for the dissolution of zirconium when the nitric acid concentration is 13M in these mixtures is 5.8 kcal/mole. The rate-controlling step during the dissolution appears to be the transport of hydrofluoric acid to the metal surface.

4. The nitric acid concentration has a pronounced effect on the average rate of dissolution over periods greater than one-half hour. An empirical treatment shows that, whereas four fluoride atoms are consumed per zirconium atom dissolved in 2M nitric acid, only two are consumed in 13M nitric acid. Therefore relatively more free hydrofluoric acid is available for further dissolution in the more concentrated nitric acid solutions, and a higher average rate of dissolution occurs than would be expected on the basis of reflux temperature alteration alone.

5. In order to minimize tin and zirconium precipitation during Zircaloy-2 dissolution at a total fluoride-to-zirconium molar ratio of 2, the nitric acid concentrations should be in the range from 5M to 8M.

6. Owing to the number of possible reaction paths for formation of gaseous products, it is not possible to ascribe a strict stoichiometry to these dissolutions.

The dissolver vessel was made of Teflon.

When pure zirconium metal is dissolved in mixtures of 13M nitric acid and various concentrations of hydrofluoric acid, the resulting dissolver solutions are stable with respect to precipitation, provided that the total fluoride-to-zirconium molar ratio is 2 or less. However, when Zircaloy-2 is substituted for pure zirconium, a precipitate occurs in this region. Since oxalate is a complexing agent for zirconium, it was thought that the addition of oxalic acid would enhance the stability of the resulting dissolver solutions. The experiments were performed using 1M to 2M nitric acid to avoid any decomposition of the oxalate. A solution initially 1M nitric, 1M oxalic, and 1M hydrofluoric acid produces a Zircaloy-2 dissolver solution that exhibits good stability, equivalent to that achieved with a solution initially 8M nitric and 1M hydrofluoric acid.

Dissolution of Zirconium Fuel Elements in Ammonium Fluoride-Hydrogen Peroxide Systems. A modified Zirflex flow sheet that involves hydrogen peroxide addition to the am-

monium fluoride solution for processing 2.5 per cent uranium-zirconium alloy fuels was proposed¹⁸ as a result of bench-scale dissolution studies. Uranium-zirconium alloy fuels containing up to 10 per cent uranium may be dissolved in 5.4M ammonium fluoride-0.33M ammonium nitrate-0.13M hydrogen peroxide.⁸ The peroxide promotes uranium solubility and suppresses corrosion of Nionel by a factor of 3 to 10 to less than 1 mil/month except at the solution-vapor interface, where it was 1 to 5 mils/month. The flow sheet for dissolution of a 7 per cent uranium-1.5 per cent tin-zirconium alloy is shown in Fig. 1.

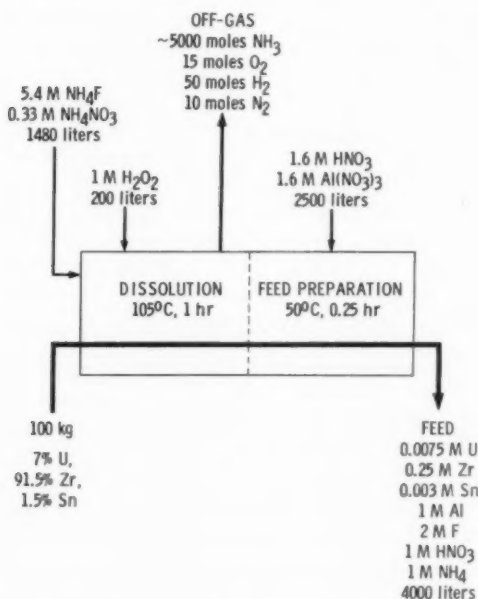


Figure 1—Modified Zirflex process⁸ for dissolution of 7 per cent uranium-zirconium alloy in NH_4F - H_2O_2 .

Dissolution of Zirconium Fuel Elements in Fused Chloride Salt. A fused-chloride-salt process under development at ICPP (ARCO process)¹⁸⁻²³ continued to look promising for the treatment of zirconium and other fuel alloys. This process employs molten lead chloride as a solvent for zirconium-uranium alloys followed by regeneration of lead chloride from the lead produced.

A tentative flow sheet for the ARCO process is based on demonstration of the quantitative leaching of uranium from a lead chloride product matrix with 8M nitric acid and regeneration

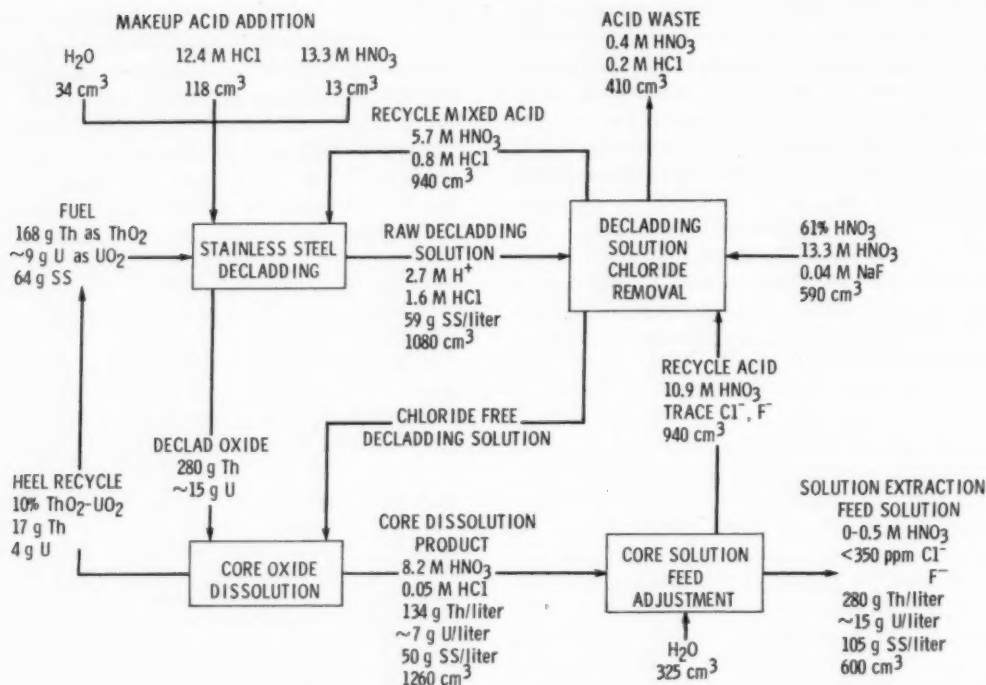
of the lead chloride by either aqueous precipitation or direct chlorination.²³ The scale of operation for the lead chloride dissolution of zirconium-uranium alloy was increased to the 100-g level without difficulty, and tests were conducted with irradiated alloy to confirm distribution of cesium-cerium to the salt phase and of ruthenium to the lead phase. Aluminum and chromium were also found to react with lead chloride. Several metals were found which were reasonably corrosion resistant. These included molybdenum, nickel, and silver metals and also an alumina ceramic.

A series of experiments was performed to determine the amount of zirconium retained in the salt phase during ARCO fused lead chloride dissolutions. During dissolution of Zircaloy-uranium alloy fuel pieces at 520°C, at least 99.8 per cent of the zirconium was volatilized.²¹

Stainless-Steel Fuel Elements. Several dissolution schemes have been proposed for stainless-steel-clad uranium or uranium dioxide. These include the Darex (dilute aqua regia) process, which may be used for complete dissolution of uranium dioxide-stainless steel fuels such as the Yankee reactor fuel. Electrolytic dissolution of stainless-steel-clad and stainless-steel matrix fuels is also being examined.

The Darex process for complete dissolution of uranium dioxide-stainless steel fuels was demonstrated in hot-cell experiments with Yankee fuel irradiated to 16,000 Mwd/ton; all operations were completely satisfactory.⁸ Fuels bonded with sodium or NaK cannot be processed by the Darex process; violent vapor-phase reactions occur between the nitrogen oxides and hydrogen. A Darex flow sheet for dissolution of CETR fuel is shown in Fig. 2.

At Savannah River¹⁴ and at ICPP (see page 39), the electrolytic dissolution of stainless steel has been studied. The stainless steel is contained in an electrolytically inert anode basket. Pressure and mechanical vibration are effective in maintaining continuous anodic dissolution in nitric acid because they help maintain electrical contact with the inert anode basket. Electrolytic dissolutions of stainless steel in nitric acid have been operated continuously for periods up to 22 hr. Contact between the stainless steel and the electrolytically inert anode basket was maintained by applying additional weight to simulate the effect of uranium dioxide cores for the slugs.

Figure 2—Darex flow sheet for CETR fuel.⁸

Al-Pu-Si-Ni Alloy Fuel Elements and Other Aluminum-Clad Fuels. Based on these more complete dissolution-rate studies, it was concluded that, when aluminum-base alloys of the types proposed for PRTR spike elements are in the active state, neither nickel nitrate nor uranyl nitrate has much effect on the dissolution rate. This is in contrast to the behavior of 2S aluminum which activates in Hg(NO₃)₂-HNO₃ solutions at higher acidity than the aluminum alloys and whose dissolution rate (when active) can be moderated significantly by the presence of nickel nitrate. Studies at HAPC^{8,10,13} have sought a better understanding of the effect of various parameters (nitric acid, aluminum nitrate, uranyl nitrate concentrations) on the dissolution of alloys proposed for PRTR spike fuels. Most work was done with an alloy having the composition (in weight per cent) 1.8 to 2.2 nickel-1.8 plutonium-0.4 (max.) iron-0.17 (max.) silicon-0.1 to 0.2 titanium-remainder aluminum. It was found that this alloy, as well as a similar alloy containing about 1 per cent silicon (on which dissolution studies were reported previously) must be in an active state to dissolve rapidly in nitric acid-mercuric nitrate solutions.

Preliminary data indicated considerably less hydrogen evolution during rapid dissolution of the 2 per cent nickel alloy than was found previously in dissolving the 1 per cent nickel-1 per cent silicon alloy.⁵ Further studies on the evolution of hydrogen during nitric acid-mercuric nitrate dissolution of proposed PRTR fuels confirmed these preliminary results.¹³ Sufficient data on hydrogen evolution as a function of nitric acid and aluminum nitrate concentrations are now available¹⁰ to permit calculation of hydrogen in the off-gas versus time for a variety of fuel dissolution schemes. The data continue to support an earlier conclusion that hydrogen evolution increases markedly as the silicon content of the alloys increases from a few tenths of 1 per cent to 1 per cent.

Composition of Off-Gases from Uranium Dissolutions. The composition of off-gases from mercury-catalyzed nitric acid dissolution of uranium alloys has been investigated at ICPP.²⁴ Off-gases usually contain hydrogen and various nitrogen oxides. A small amount of water vapor is present in the off-gas after the condenser. No dissolver sparge was used.

In full-scale pilot-plant studies of dissolution of unirradiated 7.5 per cent uranium-92.5 per cent aluminum alloy slugs in a typical plant batch dissolver, both cast and extruded slugs were dissolved. The average hydrogen concentration in the off-gas after the condenser for cast slug dissolution is 2 per cent. The maximum hydrogen to be expected for normal cast slug dissolutions (product acid concentration around 1M) is about 8 per cent. Hydrogen concentration in the off-gas in extruded slug dissolution is about 4 per cent for 1M to 2M acidic dissolver solutions, increases rapidly for acid-deficient solutions, and reaches a maximum of 23 per cent for solutions that are approximately 2M acid deficient.

The concentration of nitrogen dioxide is high in the off-gas before the condenser (above the dissolver solution) during the early part of an extruded slug dissolution but drops as the reaction proceeds. There is a sharp drop in the region of neutral dissolver solution. The average concentration of nitrogen dioxide in the off-gas before the condenser was 0.57 mole of nitrogen dioxide per mole of dry gas obtained after the condenser. The dry gas after the condenser is considered to be nitrogen dioxide free, since this constituent is almost completely dissolved in the condensate (less than 0 to 2 per cent by actual analysis).

For acidic dissolver solutions the nitric oxide concentration in the off-gas after the condenser averages 72 per cent for extruded slugs and 82 per cent for cast slugs. It decreases to 50 per cent at 2M acid deficiency for extruded slugs and 74 per cent at 0.4M acid deficiency for cast slugs.

For acidic dissolver solutions the concentration of nitrous oxide in the off-gas after the condenser averages 24 per cent for extruded slugs and 16 per cent for cast slugs.²⁵ It increases to 28 per cent at 1.6M acid deficiency for extruded slugs and to 23 per cent at 0.4M acid deficiency for cast slugs.

It may be concluded that the stoichiometry of dissolution is such that the reaction producing nitrogen dioxide diminishes in favor of the other reactions as the dissolution proceeds.

Dissolution of Dejacketed Material

Dissolution of the core is possible if fuel jackets can be removed mechanically or chemically, or it may be performed when the fuel is

sheared into pieces. Thus a simpler dissolution may be possible than when combined jacket-core dissolution is carried out.

Dissolution of Uranium-Molybdenum Alloys. Studies of the dissolution of uranium-molybdenum alloy fuel cores are being made at HAPO.^{26,27} Several of the power reactors currently being designed and constructed utilize low-enrichment (<5 per cent U²³⁵) uranium in uranium-molybdenum alloys as fuels. Special techniques are required in the dissolution of these low-enrichment uranium-molybdenum alloys to obtain feed solutions having relatively high uranium concentration and which are stable toward precipitation at low acidity. Because of the limited solubility of uranyl molybdate, dissolution of uranium-molybdenum alloy cores in nitric acid alone does not appear practical for preparation of low-acid Redox process feeds. The maximum uranium concentration attainable without precipitation of solids at a terminal acidity of 1M nitric acid is about 0.4M for uranium-3 wt.% molybdenum alloy and considerably less for 10 per cent alloy. Even lower uranium concentrations are required for stability at lower acidities.

The solubility of uranyl molybdate is increased significantly in the presence of Fe(III) nitrate.²⁶ At 1.0M ferric nitrate, for example, stable 1M uranyl nitrate-0.1M nitric acid solutions can be prepared by nitric acid dissolution of uranium-3 wt.% molybdenum alloy. Anion-exchange-resin studies indicate that a negatively charged, iron-molybdenum complex ion is present in such solutions.

Dissolution rates of uranium-3 and 9 wt.% molybdenum alloys in 1M to 5M nitric acid-0.5M to 1.0M ferric nitrate solutions are in the range 0.7 to 5.5 g/(cm²)(hr). Fe(III) catalyzes the dissolution at low acidities. Solutions obtained by nitric acid-ferric nitrate dissolution of uranium-molybdenum alloys can be stored at room temperature for long periods of time without significant precipitation of solids. Stability during storage is greater at higher acidities but is decreased as the storage temperature is increased. A chemical flow sheet for the preparation of Redox process feed stock from uranium-3 wt.% molybdenum alloy is shown in Fig. 3.

The above-mentioned flow sheet produces low-acid (<0.5M nitric acid) Redox process feeds by dissolution in ~6M nitric acid. More recent

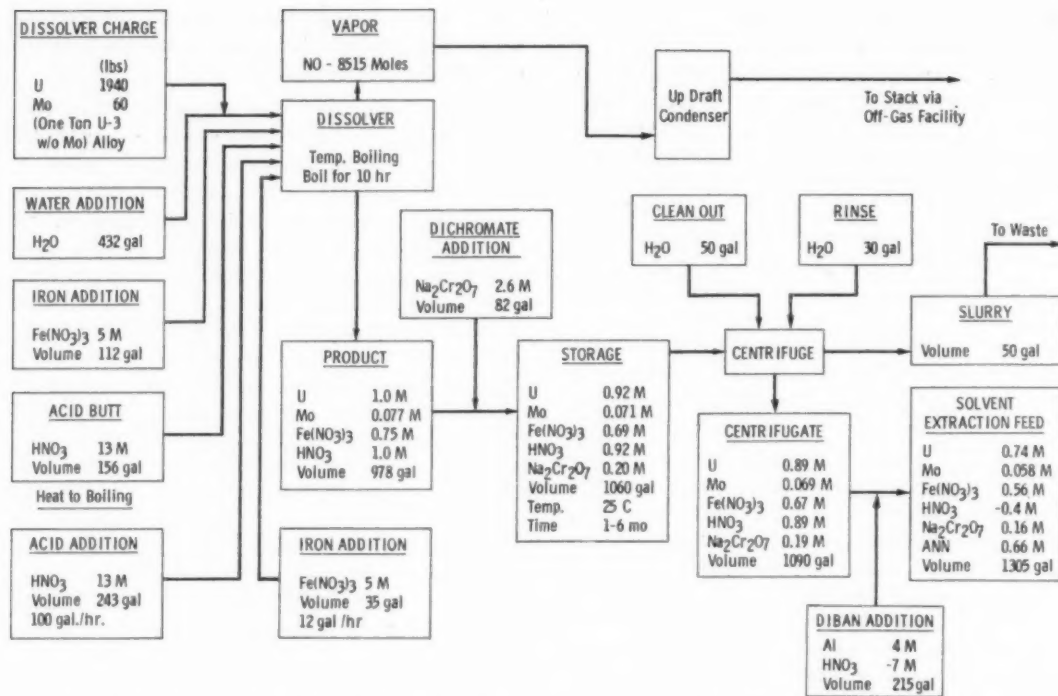


Figure 3—Chemical flow sheet for preparation of Redox process feed from uranium-3 wt.% molybdenum alloy fuel.²⁶

work at HAP0²⁷ is investigating the dissolution of uranium-3 wt.% molybdenum alloys in 12M to 14M nitric acid solutions.

Eighty to 95 per cent of the molybdenum content of uranium-3 wt.% molybdenum alloys was precipitated as white hydrated molybdic oxide when such alloys were dissolved in nitric acid. Solutions initially 12M and 14M nitric acid produced dissolver solutions of the composition 1.0M to 1.5M for 12M initial concentration and 4M to 8M nitric acid for 14M initial concentration. Approximately 90 per cent of the silicon content of a uranium-2 wt.% molybdenum-0.2 wt.% silicon alloy was precipitated under these conditions.²⁷

Molybdic oxide precipitates were bulky and did not settle well. Solid-liquid separation could be achieved by centrifugation. Centrifuged volumes of unwashed precipitates ranged from 6 to 17 vol.% for dissolver solutions 1.0M to 1.5M uranyl nitrate hexahydrate. Uranium losses to thoroughly washed precipitates were less than 0.05 per cent. The plutonium loss to the washed solid was about 2.3 per cent in the range of plutonium content studied (0.1 to 0.5 g/liter).

Plutonium and uranium values in washed precipitates were recovered by successive treatment of solid residues with caustic and nitric acid.

The acidity of solutions produced by dissolution of uranium-3 wt.% molybdenum alloys in 12M to 14M nitric acid was reduced to Redox process values (0.0M to 0.5M nitric acid) either by treatment with formaldehyde or by boildown with continuous addition of water. The former method was preferable since precipitation of a small amount of molybdic oxide occurred from both twofold-concentrated and unconcentrated dissolver solutions. Solids were not formed during formaldehyde treatment, provided that the solutions were not twofold concentrated. Solutions after either boildown or reaction with formaldehyde constituted satisfactory Redox process feed stocks.

Dissolution of uranium-10 per cent molybdenum alloy in boiling nitric acid to produce 1M uranium solutions resulted in precipitation of uranyl molybdates (e.g., uranium trioxide-2 per cent molybdenum oxide) at low acidities,⁹ from 1M to 3M. At acidities greater than 5M,

the molybdenum precipitated as molybdenum oxide (MoO_3).

Dissolution of Uranium-Graphite Fuels. At ORNL the recovery of uranium from graphite fuels is being investigated. Prototype Pebble-Bed Reactor (PBR) fuels (UC in graphite) in the form of 1.5-in.-diameter spheres (graphitized and ungraphitized, admixture type) were disintegrated to -10-mesh powder by treating with 90 per cent nitric acid either at 25°C or at boiling.^{8,9} The graphitized specimens (5 per cent uranium-graphite fuel) disintegrated more rapidly than the central core. About 84 per cent of the graphitized fuel disintegrated in 7 hr, but 24 hr was required for complete disintegration; 65 per cent of the ungraphitized fuel disintegrated in 7 hr, but only 95 per cent disintegrated after 24 hr. The powder was removed from the reaction mixture after 6 to 10 hr to avoid the formation of very fine particles which were difficult to filter. After partially disintegrated material had been washed with water, no further disintegration occurred upon subsequent treatment with 90 per cent acid. Two leaches of the powder with 90 per cent nitric acid and thorough washing with either water or nitric acid resulted in recovery of 99 per cent or more of the uranium. When complete disintegration was not achieved, only 30 per cent of the uranium was leached from the core. Grinding the PBR fuels to -4+8 mesh and leaching with boiling 70 per cent acid recovered only 97.6 per cent of the uranium.

Grinding of a silicon-silicon carbide coated ungraphitized prototype fuel sample to -200 mesh and leaching with 70 per cent nitric acid, or grinding to -4+8 mesh and leaching with 90 per cent acid, recovered 99 per cent of the uranium.⁹

In tests on disintegration of graphite fuels with bromine and interhalogens, bromine, iodine monochloride, and iodine monoboride caused swelling and disintegration of the fuels. However, uranium recoveries in leaching the residues with boiling 15.8M nitric acid were lower than those in the fuming nitric acid process but higher than those in leaching after mechanical grinding.

Nitric Acid Leaching of Stainless-Steel and Zircaloy-Clad Uranium Dioxide Chopped Fuel Rods. Nitric acid leaching of swaged uranium dioxide from stainless-steel and Zircaloy-clad uranium dioxide chopped fuel rods $\frac{1}{2}$ in. in

diameter was investigated at HAP0¹⁰ on laboratory and pilot-plant scales. The difference in uranium dioxide dissolution times for elements having different lengths was determined. One-, two-, and three-inch-long sections of swaged uranium dioxide rod clad with Zircaloy were leached with 6M nitric acid at a nitric acid/uranium charge ratio of 5. Dissolution was complete in every case in less than one-half hour. This fast dissolution time is attributed to erosion of the uranium dioxide from the cladding, which resulted in high surface area exposure.

Precipitation Processes

Precipitation processes have been proposed for head-end treatment in preparation for solvent extraction. A recently declassified report²⁸ discusses a potassium permanganate-manganese dioxide head-end procedure for the removal of ruthenium and niobium-zirconium prior to a Purex solvent-extraction process. Work at Savannah River on an improved method for precipitating manganese dioxide is reported.²⁹

The Savannah River modification of the potassium permanganate-manganese dioxide head-end procedure was shown to increase the processing capacity of the Purex head-end step significantly.²⁹ The equipment modifications to produce the manganese dioxide precipitate were: (1) a shroud mounted around the upper of two paddles in the precipitation tank, (2) a line to feed potassium permanganate solution into the shroud, and (3) an increase in the agitator speed. The results obtained are summarized below:

1. The precipitate could be centrifuged at five times the rate that could be obtained with the precipitate formed by the older method.

2. The precipitate formed at 160°F by the new method could be centrifuged as readily as that produced at 190°F. Operation at lower temperatures is desirable to reduce volatilization of ruthenium.

3. The total capacity of the centrifuge bowl was increased as a result of the increase in precipitate density, and the resulting cake could be washed more efficiently. Three cake washes were necessary for a cake of normal size; five washes were necessary when the size of the cake was doubled.

4. The cake was readily slurried from the centrifuge bowl and remained in suspension

while the slurry was discharged through piping that simulated a waste-disposal header.

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Section IV

RESEARCH AND DEVELOPMENT ON FUEL PROCESSING

Solvent Extraction

Modifications of the Purex

and Redox Processes

With few exceptions irradiated reactor fuels are processed by either the Purex (tributyl phosphate extractant) or Redox (methyl isobutyl ketone extractant) solvent-extraction processes for the separation, purification, and recovery of uranium, plutonium, and thorium. Current Purex and Redox development work is devoted to the processing of a large variety of nonproduction reactor fuels or to the improvement of the basic processes.

Some success has been realized on a laboratory scale in the development of a Purex type process for the recovery of uranium from phosphoric acid solution. Phosphoric acid feeds are not suitable for conventional Purex processing because of the presence of difficultly extractable U(VI) and Pu(IV) complexes. Uranium was satisfactorily recovered from a Los Alamos fuel solution originally containing 0.327M uranium and 18.05M phosphoric acid. A suitable solvent-extraction feed was prepared by adjustment of the feed to 1.6M ferric nitrate and 0.05M sodium nitrate to form a ferric phosphate complex. Uranium was extracted quantitatively with 6 per cent tributyl phosphate (TBP) in kerosene; however, only 3 per cent of the plutonium was extracted, scrubbed, and stripped with the uranium.¹

Additional uranium distribution data are available relative to the Purex processing of feed solutions prepared by the ammonium fluoride dissolution of zirconium-uranium fuel. Ammonium nitrate salting was studied for extractants containing 5, 10, and 20 per cent TBP. Figure 4 shows the effect of the ammonium nitrate salting strength on the uranium distribu-

tion coefficient. With high salting strength, extraction coefficients in excess of 1000 were obtained.²

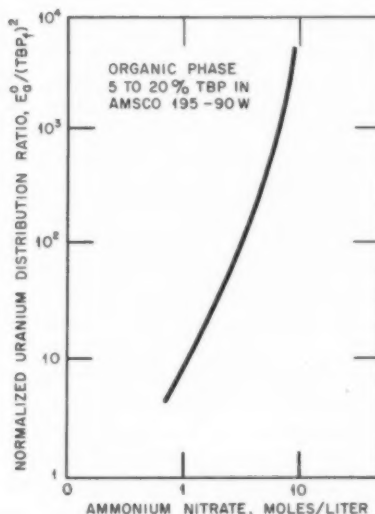


Figure 4—Uranium extraction from ammonium nitrate.²

Feed solutions prepared by ammonium fluoride dissolution unavoidably contain some free fluoride ion. Uranyl ion forms a relatively stable difficultly extractable fluoride complex. The effect of fluoride ion can be partially overcome by the addition of nitric acid, but there remains a substantial hindrance to extraction by TBP as shown by the data in Table IV-1. Studies are in progress on the extraction of uranium with 10 per cent TBP from a solution containing 3.9M ammonium nitrate and 1M nitric acid. Addition of hydrofluoric acid to the 3.9M ammonium nitrate-1M nitric acid dissolver solution reduced the uranium distribu-

Table IV-1 SALTING EFFECT OF AMMONIUM NITRATE ON URANIUM DISTRIBUTION COEFFICIENTS

(Organic Phase: TBP; Aqueous Phase: NH_4NO_3 with HNO_3 and F^- Additions)

Uranium distribution coefficient, E_a^0			
6M NH_4NO_3 only	6M NH_4NO_3 , 2.6M HNO_3	6M NH_4NO_3 , 0.1M F^-	3.9M NH_4NO_3 , 1M HNO_3 , 0.1M F^-
108	~10	0.26	~5

tion coefficient from 28 with no hydrofluoric acid to values of 18, 5, and 0.5 with the additions of 0.01M, 0.1M, and 0.5M hydrofluoric acid, respectively.

Polish investigators have published data on the extraction of thorium, zirconium, cerium, promethium, and yttrium from perchloric acid solutions with pure TBP. In general, high distribution coefficients for all trivalent and tetravalent cations were noted at high acidity. For example, the distribution coefficient for zirconium varied from 0.0018 at 3.42M acid to >5000 at 9.27M acid. At all acid concentrations,³ separation factors were about unity for various rare earths—yttrium and about 70 for thorium-zirconium.

Purex processing achieves relatively poor decontamination of ruthenium and zirconium-niobium activities. A "tail-end" treatment of aqueous product streams with silica gel provides satisfactory decontamination from zirconium-niobium activity. Ruthenium remains as the most troublesome contaminant in routine Purex processing. Numerous studies of ruthenium compounds and their behavior in Purex processing show that there exists a number of stable nitrosyl ruthenium nitrates which are readily extracted by TBP. Nitrosyl ruthenium dinitrate, however, is relatively poorly extracted by TBP. Recent investigations of methods to convert the higher nitrates to the dinitrate have met with some success. Studies have been made of the effect on ruthenium extractability of the treatment of aqueous feed solution with nitrogen dioxide and nitrogenous gases produced by dropping sulfuric acid into a solution of sodium nitrate. The effectiveness of the treatment was determined by contacting the treated aqueous phase with 20 per cent TBP. Treatment with nitrogen dioxide was not very effective. Treatment with nitrogenous gases resulted in a 50

per cent decrease in the ruthenium distribution coefficient.⁴

Studies of Alternate Extractants

A number of organonitrogen and organophosphorus compounds are excellent extractants for uranium. Originally, process interest in these extractants was directed toward the recovery of uranium from ore leach liquors. More recently, interest has developed in the application of these versatile and highly selective extractants to the processing needs of some of the nonproduction reactor fuels.

ORNL is responsible for most of the basic work and process development involving these extractants. Recent work in this field is reviewed in their annual progress report. A summary of some of the more interesting developments is presented⁵ in Table IV-2.

An important application of organophosphoric acids is the recovery of selected fission products from Purex aqueous waste. In a laboratory-scale demonstration, 99 per cent of the strontium and 95 per cent of the rare earths were extracted from an adjusted Purex waste solution with a synergistic mixture of 0.3M di-2-ethylhexyl phosphoric acid (D2EHPA) and 0.15M TBP in Amsco 125-82. A suitable feed solution was prepared from the aqueous waste by adding 1M tartrate and sodium hydroxide to give⁶ a pH of 6. Costripping of strontium and rare earths with 2M nitric acid yielded first-cycle decontamination factors of 24 for ruthenium and 9 for zirconium-niobium. A second-cycle feed was prepared by adding 0.005M tartrate and sodium hydroxide to give a pH of unity. Extraction of rare earths with the synergistic mixture of di-*sec*-butylphenyl phosphonate (D-*s*-BPP) and TBP followed by stripping with 2M nitric acid yielded a rare earths to strontium separation factor in excess of 10^4 . Adjustment of the pH of the second-cycle raffinate to 6 and stripping with 2M nitric acid yielded a strontium product with a strontium to rare earths separation factor of 10^3 .

A systematic investigation of the application of several organonitrogen compounds to nuclear fuel processing problems is in progress at Massachusetts Institute of Technology. Compounds of current interest are ditridecylamine (DTDA), trilaurylamine (TLA), and Primene JMT. A modifier, usually primary decyl alcohol (PDA), is added to the amine to increase the

Table IV-2 SOME PROCESS APPLICATIONS OF ORGANOPHOSPHORUS AND ORGANONITROGEN COMPOUNDS⁵

Extractant	System treated	Values recovered	Other comments
Quaternary ammonium compound	Carbonate solution from ore processing	Uranium	Excellent uranium recovery in laboratory tests; impurities interfered in pilot test with plant liquor
0.5M mono-2-ethylhexyl ortho-phosphoric acid	10M lithium chloride	Separation of rare earths and americium	> 90 per cent extraction of neodymium and cerium; 0.04 per cent americium loss
Di-sec-butylphenyl phosphonate	Thorex process product concentrate	Uranium-thorium separation	Separation factor 34 times that obtained with TBP; quantitative uranium recovery with thorium decontamination factor of 250; uranium-D-s-BPP and thorium-D-s-BPP complexes were soluble in carbon tetrachloride
0.1M to 0.3M primary amine	Sulfuric acid-stainless steel cladding solution	Uranium and plutonium	Consecutive extraction of U(IV) and Pu(III) or Pu(IV)
Dialkylphosphoric acid	Sulfuric acid-stainless steel cladding solution	Uranium	Plutonium goes to waste stream

solubility of extracted species.⁷ Some recent findings of this program are as follows:

1. The solubility of nitric acid in Amsco-diluted amine was increased substantially by the addition of PDA.

2. In extraction of zirconium with 0.35M TLA, distribution coefficients varied from 7.1×10^3 in 10.3M nitric acid to 0.12×10^3 in 2M nitric acid. The addition of 10 to 20 per cent PDA had little effect on the distribution coefficient.

3. With 0.33M Primene JMT, the zirconium distribution coefficient was 6.3×10^3 in 9.8M nitric acid and 0.05×10^3 in 1.7M nitric acid.

4. The distribution coefficients for ruthenium extracted with TLA and DTDA were time dependent.

The time dependence of the ruthenium distribution is of particular interest. Starting with aged nitrosyl ruthenium nitrate solutions in 2M and 6M nitric acid, extractions were made at contacting times of $\frac{1}{2}$ to 95 hr. As shown by the data in Table IV-3, the coefficient increased by an order of magnitude as the contact time was increased from $\frac{1}{2}$ to 95 hr. A zirconium-ruthenium separation factor in excess of 10^3 may be obtained in extraction with TLA.

Radiation Damage to Process Extractants

Considerable interest has developed in the use of Solvesso-100 as a replacement for Amsco

Table IV-3 EFFECT OF CONTACT TIME ON RUTHENIUM DISTRIBUTION COEFFICIENT, E_a^0

(Organic Phase: 0.42M Trilaurylamine; Aqueous Phase: 1.54 g of Ruthenium per Liter in 6.0M Nitric Acid)

Contact time, hr	Ruthenium distribution coefficient, E_a^0
0.5	0.021
1	0.026
5	0.27
95	0.29

125-82 (kerosene) as the Purex diluent because of its apparent superior radiation resistance. Not only is Solvesso-100 more resistant to radiation damage, but it also appears to retard the radiation-induced decomposition of TBP measured in terms of organic acid production.⁵ TBP-Solvesso-100 is 2.5 to 3 times more resistant to radiation damage than TBP-Amsco 125-82 (as measured by G values of 0.25 versus 0.72 molecule of monobasic acid formed per 100 ev). Solvesso-100 is an aromatic compound. The protective effect of the benzenoid structure is known and has been studied in connection with organic-moderated and -cooled reactors. In general, the studies of Burr and Strong⁸ have shown that the relative yields of gas and polymer for aromatic hydrocarbons are roughly inversely proportional to the number of benzenoid rings linked together.

Fundamental Studies

The development of laboratory tests that can be correlated with actual extraction-column performance has been the subject of considerable study. Unfortunately, these efforts have in the past met with little success. Recent developments in this area are encouraging, and improved procedures are now available for estimating contactor performance and scaleup parameters from laboratory data.

In Purex processing, a need exists for relatively simple tests that will afford accurate prediction of such factors as column capacity and product losses and decontamination. Apparently no practical method exists for predicting the dispersion and coalescence characteristics of aqueous-organic systems. For several years the National Lead Company of Ohio has been studying this problem at its feed materials center. In an experimental program initiated to evaluate used Purex solvent, the following three tests were developed and are now in routine use at the National Lead refinery:

1. A reextraction test to establish the levels of dibutyl phosphate (DBP) and other uranium complexing agents.
2. A coalescence time measurement to measure emulsification tendencies of the system.
3. An infrared spectral analysis of the solvent to measure the extent of kerosene-diluent degradation.⁹

Coalescence-time measurements were obtained under standardized conditions by measuring the break times of emulsions generated in 50-ml cylinders containing 25 ml of a standard uranyl nitrate solution and 25 ml of the solvent under observation. With fresh solutions, excellent reproducibility was obtained. A typical curve showing break time as a function of aqueous-phase uranium concentration is provided in Fig. 5.

A more pertinent point, however, is the emulsification tendencies of actual process streams. In most cases the formation of interfacial residues prevented a clean break of the phases. An arbitrary decision, redefining the break time as the coalescence of a certain amount of emulsion, was used to provide a basis for comparing fresh and used solvents. These comparisons showed substantially longer break times for used solvent than for fresh solvent. Typical results are presented in Table IV-4.

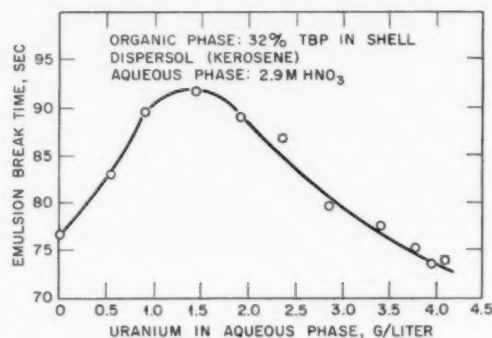


Figure 5—Stability of emulsions produced with fresh solutions.⁹

Table IV-4 COMPARISON OF EMULSION BREAK TIMES FOR FRESH AND USED PUREX SOLVENT⁹

(Aqueous Phase: 2.8M Nitric Acid, 190 g of Uranium per Liter; Organic Phase: 33.5 Per Cent TBP in Kerosene)

Solvent source	Break time, sec
Freshly prepared	89
Process stream	325
Discarded solvent	> 600

The infrared spectral analysis afforded detection of isoparaffinic hydrocarbons, TBP-nitric acid complexes, uranium, water, and evidence of diluent degradation products such as organic acids and organonitrogen compounds. Measurements were obtained using a potassium bromide cell at a path length of 0.05 or 0.25 mm. Specimens were scanned from 1 to 15 μ to detect TBP-nitric acid complex, uranium, and water. Scans over the range of 2 to 7 μ were used to detect diluent degradation products.

The role of surfactants in emulsion formation and coalescence is not clearly understood. Excessive emulsification in Purex facilities has frequently been attributed to the presence of surface-active contaminants. In the recovery of uranium from ore, the tendency for emulsion formation in TBP extraction of uranium concentrates can be decreased by the presence of certain surfactants. Uranium concentrates prepared by nitric acid digestion contain insoluble suspended solids. Experiments have shown that the addition of surfactants, which presumably are adsorbed on the solids, reduces the emulsification tendencies of the system.¹⁰

It has frequently been observed that an emulsion may be broken by effecting a phase inversion. The uranium concentrates were normally processed in an oil-water system. It was assumed that the role of an effective surfactant is to make the solids organic wettable and thus promote phase inversion from oil in water to water in oil. TBP apparently is such a surfactant because, for various refinery conditions, an increase of the TBP concentration of the extractant decreased the emulsion problems.

A terminal report providing details of a well-executed study of the design and scaleup of mixer-settlers for the Dapex process has been published.¹¹ The Dapex process employs a synergistic mixture of di-2-ethylhexyl phosphoric acid and TBP in kerosene to recover uranium from sulfuric acid ore leach liquor. Uranium is stripped with sodium or ammonium carbonate. The development of parameters valid for a 200-fold scaleup of mixer-settlers was reported previously.¹² The discussion herein deals with some of the more fundamental studies that were a part of the over-all program.

The kinetics of uranium transfer were studied¹¹ in 6- and 12-in. continuous-flow contactors at individual flow rates from 0.15 to 5 gal/min. Preferential sampling of one phase of an emulsion was required to establish mixer efficiency. The design of samplers which would pass one phase and filter out the other was based on the wetting characteristics of glass and Teflon frits. Glass frits were preferentially wetted by the aqueous phase, whereas Teflon frits were preferentially wetted by the organic phase. Table IV-5 presents some typical sampling data and shows that the dispersed-phase sample apparently provides a more accurate measure of the actual solute concentration than does the continuous-phase sample.

Mass-transfer coefficients for uranium transfer were measured in a 6-in. continuous-flow contactor.¹¹ Interfacial areas required to calculate the mass-transfer coefficient were estimated from a published correlation.¹³ Although the product ka (the product of the mass-transfer coefficient and the interfacial area) was a function of flow and mixing parameters, surprisingly the mass-transfer coefficient (k) showed negligible variation, being between 5.0×10^3 and 6.0×10^3 cm/min for all conditions studied. The mass-transfer coefficient was also measured in a laboratory contactor with a quiescent interface of fixed area, and a value of 5.4×10^3 cm/

Table IV-5 EVALUATION OF EMULSION SEPARATION BY POROUS FRITS¹¹

(Direction of Uranium Transfer: Aqueous to Organic)

Aqueous phase g of U per liter		Organic phase g of U per liter		
Glass frit	Settled effluent	Teflon frit	Calculated by material balance from glass-frit data	Settled effluent
<i>Oil in Water Emulsion</i>				
3.6	3.2	0.84	1.9	2.3
2.5	1.9	1.6	2.8	3.4
2.1	1.3	2.4	3.2	4.0
<i>Water in Oil Emulsion</i>				
4.7	3.2	1.7	1.2	2.7
3.8	1.3	3.0	1.7	4.2
2.9	0.9	3.4	2.5	4.5

min was noted. Specific areas (interfacial area divided by the volume of the system) of the two contactors differed by a factor of 4000. The agreement observed is particularly significant because this is the first published experimental data comparing coefficients for mass transfer between phases of an emulsion in continuous flow and for mass transfer across a fixed interface in a static system.

Ion-Exchange Processes

Recovery and Purification

of Americium, Curium, and Promethium

Development of anion-exchange procedures for separating actinides and lanthanides continued at ORNL.

A process for separation of americium and curium from rare earths by anion exchange based on selective chloride complexing has been developed and tested on a laboratory scale at ORNL with tracer amounts of Am^{241} and Cm^{242} and macroamounts of mixed rare earths.¹⁴ This process is a modification of the process reported in an earlier Review.¹² The separation is accomplished by sorption of americium, curium, and rare earths on Dowex 1-10X resin from a solution of 8M lithium nitrate followed by selective elution of rare earths with 10M lithium chloride and americium-curium elution with 1M lithium chloride. Laboratory demonstration of this process has given greater than

99.5 per cent recovery of americium tracer containing no detectable amounts of rare earths.

At ORNL 20,000 curies of Pm^{147} in a mixture of rare-earth fission products was processed by ion exchange on a cation resin, using ammonium citrate solution as the eluant.¹⁵ Promethium was present to the extent of about 1.6 per cent in the starting mixture and was increased to 60 per cent in the final product.

Miscellaneous Ion-Exchange Studies

Ion-Exchange Purification of Reactor Cooling Water. Development work continues on an ion-exchange process for pH control and removal of radioisotopes from a pressurized-water reactor system¹⁶ (Shippingport). The pH of circulating coolant systems can be effectively and conveniently controlled in the range pH 9.5 to 10.5 by the use of mixed-bed ion-exchange resins in the lithium hydroxide or potassium hydroxide form if water makeup rates are not too high. Lithium is more easily displaced from lithium hydroxide resin than potassium is from potassium hydroxide resin. This is especially true with respect to displacement by any ammonium ions that may be produced in the coolant by radiation reactions. Thus the pH may be more easily controlled by lithium hydroxide resin than by potassium hydroxide resin when water makeup rates are high.

The reactions of ion-exchange resins and hydrogen peroxide have been examined by Baumann¹⁷ in relation to the performance of ion-exchange resins in maintaining water of high purity for nuclear reactors. Hydrogen peroxide is produced by irradiation of coolant water. The interaction of the following resins with peroxide was investigated: Amberlite* IR-120-H, IRA-400-OH, IRA-400-CO₃, IRA-400-HCO₃, IRA-400-Cl, and XE-150. Of these, only IRA-400-OH and XE-150 (a mixed resin that contains purified IRA-400-OH) reacted appreciably with dilute peroxide, although some damage to the resin matrix of IR-120-H occurred with 30 per cent hydrogen peroxide. Up to 15 per cent of the strongly basic exchange sites in IRA-400-OH could be converted to weakly basic sites by repeated contact with 0.5M hydrogen peroxide. In addition to the chemical attack observed, peroxide was absorbed by IRA-400, especially

in the hydroxide form, even from very dilute ($10^{-4}M$) solutions. This was apparently an ion-exchange process in which the resin was converted to the hydroperoxide form. The equilibrium quotient* was about 1.5 at 25°C. The absorbed peroxide decomposed with the evolution of oxygen and the regeneration of the hydroxide form. The decomposition was first order at concentrations above about 0.2 mole hydrogen peroxide/equivalent of resin. Below this, the rate increased abruptly, and no kinetic interpretation was attempted. The half life of the first-order decomposition at 30°C was 0.7 hr for IRA-400-OH and 1.6 hr for XE-150. The apparent activation energy was about 20 kcal/mole for both resins.

The laboratory observation that only the hydroxide form of the resin absorbed peroxide to any great extent was confirmed in a miniature purification loop. When irradiated water was passed through beds of mixed resin in the H-OH and H-CO₃ forms, peroxide was removed only by the H-OH bed.

The conclusions from this work may be summarized as follows:

1. Peroxide concentrations of a few parts per million, such as would occur in irradiated water, will not harm ion-exchange resins or affect the ion-exchange process to any great extent. The anion resin in the hydroxide form will remove the peroxide; the absorbed peroxide will decompose, stoichiometrically releasing oxygen and regenerating hydroxide resin. This means that some gassing will occur in the column; at higher concentrations of peroxide, this gassing might affect column operation.
2. Significant amounts of products other than oxygen, such as carbon dioxide, will not be produced, although trace amounts of organic material may be released which could produce carbon dioxide through subsequent irradiation.
3. The ability of the column to remove other ions will be affected slightly, if at all, by the presence of peroxide in the system, since the affinity of the resin for peroxide is less than that for most other anions.
4. As the column becomes saturated with other anions, its ability to remove peroxides by ion exchange will decrease. Therefore the per-

* Trademark, Rohm and Haas Co., Philadelphia, Pa.

* $K_e = [(\text{millimoles of } \text{H}_2\text{O}_2 \text{ in resin}) / (\text{exchange capacity of resin} - \text{millimoles of } \text{H}_2\text{O}_2)] \times [(\text{molarity of OH}) / (\text{molarity of } \text{H}_2\text{O}_2)(\alpha, \text{ the degree of dissociation of } \text{H}_2\text{O}_2)]$.

oxide content of the solution may increase, although the presence of absorbed metal ions may catalyze peroxide decomposition and effect removal in this way.

5. The net result of a process in which peroxide is formed by radiolysis of water and then removed by ion exchange will be to produce stoichiometric amounts of hydrogen and oxygen from the water.

Capacity of Dowex 21K for Uranyl Sulfate. Dowex 21K anion-exchange resin has been proposed for one step of a process for the production of uranium tetrafluoride from sulfate ore leach liquors.¹⁸ Further measurements of the rate of uranyl sulfate loading on sulfate- and nitrate-equilibrated Dowex 21K anion-exchange resin have been made at ORNL by a single-bead technique.⁵ The data were used to calculate apparent uranium diffusion coefficients by considering the process as simple diffusion into a sphere. These coefficients appear to be nearly independent of the loading solution concentration over the range studied but dependent on the particle size of the resin used. The coefficients observed during loading on sulfate-equilibrated 1200-, 960-, and 820- μ Dowex 21K were 1.3×10^{-7} , 0.76×10^{-7} , and 0.49×10^{-7} cm²/sec, respectively. Self-diffusion coefficients for sulfate ions in the resin were $(1.27 \pm 0.25) \times 10^{-6}$, $(0.60 \pm 0.18) \times 10^{-6}$, and $(0.75 \pm 0.17) \times 10^{-6}$ cm²/sec for 1200-, 960-, and 820- μ resin, respectively.

A device was designed and constructed for contacting samples containing several beads to eliminate data scatter (20 to 25 beads required) caused by variation in capacity of individual beads.^{5,19} The uranium self-diffusion coefficient in 1200- and 960- μ resin was determined to be 4.4×10^{-8} and 2.6×10^{-8} cm²/sec, respectively; the apparent uranium diffusion coefficients observed during nitrate and chloride elution were 1.8×10^{-7} and 2.38×10^{-7} cm²/sec, respectively.

Development of Ion-Exchange Equipment. Development of new types of ion-exchange equipment continues at Hanford.²⁰⁻²² This was discussed in the previous Review.²³

Shakedown studies were completed in the prototype continuous multistage agitated-bed ion exchanger (MABIE) contactor which is a 6-in.-diameter by 11-ft-long dual-purpose column with seven loading and three scrub stages and a 6-in.-diameter by 12-ft-long elution column with six stages.²² An aqueous flow rate of

280 gal/(hr)(sq ft) was obtained in the adsorption column at an agitator speed of 530 rpm. The aqueous flow was limited by the power available to drive the agitator.

Sodium breakthrough runs indicated some aqueous channeling. Mixing efficiencies of 76 and 83 per cent were obtained at aqueous flow rates of 115 and 225 gal/(hr)(sq ft), respectively. The lower efficiency of the prototype contactor, as compared to the nearly perfect mixing obtained in the three-stage contactor, is attributed partly to the lower agitator speed (470 rpm versus 670 rpm) and partly to agitator design and scaleup.

Studies were made with both columns operating together to develop an effective method of minimizing the carry-over of "slip water" with the resin from one column to the other and to control the intercolumn resin flow rate. Carry-over of excessive high-acid slip water from the adsorption column to the elution column would result in a high-acid product stream and would also lower the elution efficiency. A 4-in.-diameter by 12-in.-long "disengagement" pot was installed between the lower ends of the columns. Initial studies show good performance both in limiting acid carry-over and in controlling the resin flow.

In analyzing the mass-transfer efficiency of the MABIE contactor, the assumption has been that each stage acts as a separate, perfectly mixed vessel.²⁰ There was some question, however, as to the validity of this assumption. If the mixing characteristics of the contactor are unpredictable and are limiting the over-all efficiency, any data from a pilot-plant contactor are of doubtful utility in designing a full-scale unit. However, if the mixing characteristics are predictable and the mass transfer is the controlling factor, the mixing can be taken into consideration in designing a full-scale unit.

In analyzing the mixing characteristics of the MABIE contactor, a mathematical model expressing the concentration-time relation for a perfectly mixed vessel has been expanded to apply to a contactor containing many stages in which no reaction or mass transfer is taking place. The theoretical behavior of a three-stage contactor was calculated and compared with the measured data obtained from a run in the experimental three-stage contactor. The stage void volume, flow rate, and solute concentration were the same for both the experimental run and the calculated curve. At an

aqueous flow rate of 290 gal/(hr)(sq ft), the experimental curve was of identical shape to the calculated curve and displaced by an amount equivalent to the quantity of solute taken up by internal solution in the resin. This indicates the validity of the mathematical model and allows its use for quick and quantitative analysis of actual agitated-bed performance.

A Jiggler (jigged-bed continuous counter-current ion exchanger) contactor is being developed at Hanford²⁰⁻²² as reported in previous Reviews.^{12,23,24} Flow-sheet runs²³ showed the need for equipment modifications.

A new intermediate section between the absorption and elution columns has been installed and tested.²⁰ The section is 4 in. in diameter and thus provides a completely open transfer channel. A screen near the bottom of the new section provides exit for the raffinate and, as before, restricts the pulse effect to the absorption column only. The pressure drop across the column is practically zero.

Tests also indicated²⁰ that the use of air or a combination of air and water to recycle the resin may not be adequate for controlling the flow rate or for effecting sufficient separation of resin from slip liquid at flow-sheet requirements of about 200 cm³ of resin per minute. Attempts to introduce water to assist the air have increased the quantity of resin recycled but have not in initial experiments sufficiently reduced the strength of the 7M nitric acid slip liquid which is carried into the elution column with the resin. A small d-c drive centrifugal pump was then used in place of an air lift to transfer resin to the top of the C column. The pump successfully transported wet settled resin (not pulsed) at a controlled constant rate through 5 ft of 3/8-in. tubing against a head of 2 ft. The flow range was from 297 to 1243 ml/min.

Visual observations indicated²¹ that the 1/2-ft scrub section was probably too short and was contributing to excessive fluidization at the bottom of the A column. It was replaced by a 3-ft section which gave the apparatus a more realistic 1 to 1 ratio—A section to scrub section. Tests showed this helped to stabilize operation of the A column. The greater mass of resin and the greater distance between the scrub and feed entry points are characteristics of the longer section which tend to reduce turbulence and fluidization. Redesign of the resin cycle cone, which is an inverted hollow cone or essentially

a funnel at the bottom of the A column, also improved column operation.

Three runs, ranging from 5 to about 11 hr in duration, were made with thorium-containing feed.²² Thorium is used as a stand-in for plutonium. Waste losses ranged from 16 to about 57 per cent. These high losses are attributed to improper aqueous downflow from the C column resulting either from inefficiency in that column or from downflow of a part of the product stream due to a malfunction of the flow-control arrangement.

Tests to evaluate the stability of the semi-fluidized moving bed of the Jiggler contactor were continued.²¹ One requirement for stable steady-state operation of the Jiggler is a constant rate of resin removal from the bottom of the A column. Continual removal of resin permits additional resin to settle into the recycle cone during the relaxation stroke of the pulser. The resin is then forced through the recycle line by the compression stroke of the pulser. Steady state as manifested by about a 3/4-psi drop across the semifluidized bed in the adsorption section and a constant resin level in the elution column was reached in 30 to 45 min after startup from a dense resin bed.

Kinetics of the adsorption of thorium nitrate complex ions on the Permutit SK anion exchanger were studied at HAPO.^{21,22} The data are desired as a basis for using thorium nitrate as a stand-in for plutonium nitrate during evaluation of operating characteristics of continuous ion-exchange contactors. Rates of adsorption of thorium from nitric acid solution onto Permutit SK (20 to 50 mesh) anion-exchange resin at room temperature from 5M, 6M, and 7M nitric acid at thorium concentrations ranging from 0.2 to 12 g/liter were determined.^{21,22} Data obtained fit the proposed theoretical model for adsorption. Diffusion coefficients ranged from 7.2×10^{-9} to 14.4×10^{-9} cm²/sec for the nitric acid and thorium nitrate concentrations studied. The following equation was derived which gives the distribution coefficient (K_D) as a function of resin loading:

$$K_D = \frac{K(1 - 2x)^2}{(1 - x)}$$

where x = (moles of thorium per unit weight of resin)/[total exchange capacity of resin (equivalents per unit weight)/2] and K = a constant.

Special techniques for ion-exchange separations have been reported by Tremillon²⁵ and Gorsuch²⁶ and at Aero projects.²⁷

Volatility Processes

The volatility of uranium and plutonium hexafluorides has been proposed as a basis for processing various types of irradiated fuels. Liquid-phase fused-salt processes are being considered for application to the recovery of uranium from molten-salt reactor fuel and from zirconium-uranium alloy fuel. Solid-phase-gas phase fluorination processes have also been proposed for application to zirconium-uranium alloy fuel and to uranium dioxide fuels. Fluidization techniques are employed in these dry halogenation processes to enhance process control. Applications to plutonium-bearing fuel are also being studied.

Fused-Salt Processes

In the fused-salt process for recovery of uranium from zirconium-matrix alloy fuels, being developed at Argonne National Laboratory (ANL) and ORNL, the alloy is dissolved in a molten fluoride mixture at 500 to 700°C with a hydrogen fluoride sparge, and then uranium hexafluoride is volatilized with a fluorine sparge.

A practical problem in this process has been the corrosion of metal vessels. One effort to eliminate corrosion in the primary dissolution step has been the use of a graphite-lined dissolver-hydrofluorinator. A series of fused-salt dissolutions of synthetic zirconium-uranium fuel assemblies was carried out in the pilot-plant graphite dissolver at ANL. Batch dissolutions were made according to a semi-continuous flow sheet with partial salt removal and periodic additions of sodium fluoride make-up after each run. Dissolution rates in the sodium fluoride-zirconium fluoride mixture under hydrogen fluoride sparge have been as high as 3.4 mg/(min)(cm²), resulting in a 90 per cent dissolution of the approximately 90-mil-thick plates in less than 5 hr. Satisfactory operation of the internal graphite heaters and other components exposed to the molten salt have been obtained over 1600 hr of accumulated exposure in continuing tests.²⁸

Ordinary grades of commercial graphite have a porosity of about 20 per cent and considerable permeability to fluids. Consequently, designs

using such graphite have employed a frozen-wall principle to provide fused-salt containment. The graphite dissolver undergoing tests at ANL^{12,23} is of this type. However, newly developed impregnated graphites in a wide range of structural sizes and forms make possible designs of graphite components with high resistance to molten-salt penetration. In continuing tests at ORNL, penetration of graphite by molten lithium fluoride-beryllium fluoride-thorium fluoride (a molten-salt-reactor blanket composition) at approximately 700°C and 70 psig showed weight gains of 21 per cent for a typical standard grade of graphite and as low as 0.1 per cent for special low-porosity grades.²⁹

Chemical attack of graphite by fused fluoride-hydrogen fluoride environment has appeared negligible in practical operation at ANL.¹² As part of a general survey of graphite compatibility with molten halides, studies of the formation of intercalation compounds is under way at ORNL. Graphite has a structure consisting of planes of carbon atoms and forms lamellar or intercalation compounds with halogens and halides, the atoms of which are deposited between the carbon planes. The distance between the planes is increased by such reactions, and the graphite as a whole is subject to swelling and disintegration. These effects have not been apparent in practical fused-salt processing. In the present study of intercalation compounds in molten halide systems at ORNL, appreciable attack of graphite occurred only with concentrated ferric chloride and at relatively low temperatures (300°C). Higher temperatures and dilution minimize the attack. No evidence of attack with fuel or breeder fluoride salts or with fission-product fluorides has been found.⁴

Further details of previously cited ORNL work have been reported for both laboratory^{5,30} and pilot-plant-scale^{5,31} process demonstrations. Nickel and a nickel-molybdenum alloy, INOR-8, are used as construction materials. The hydrofluorination experiments, according to the flow sheet published earlier,³² in the INOR-8 prototype of the ORNL pilot-plant hydrofluorinator demonstrated satisfactory dissolution rates, about 1.23 mg/(min)(cm²), with initial and final temperatures of 650 and 500 to 550°C, respectively. General corrosion of the vessel was not detectable by Vidigage inspection (ultrasonic thickness detector) after 74.5 hr of hydrogen fluoride exposure at 550 to 650°C. A single point at the interface level had corroded

at a rate of about 0.4 mil/hr. Complete dissolution of Zircaloy-2 elements was demonstrated.⁵

Finely divided metallic particles, thought to be the result of the reduction of fluoride impurities (fluorides of metals such as nickel, tin, chromium, molybdenum, and iron), were present as a result of corrosion of the dissolver vessel and dissolution of Zircaloy-2. Observations made during the 10 current runs, as well as during earlier runs in copper-lined equipment, indicated that a reaction takes place between metal fluoride salts and metallic zirconium and hydrogen. Some of the metals produced by reduction adhere to the surface of the zirconium, decreasing the exposed surface and thus the dissolution rate. Some of the reduced metal is dispersed into the salt, where it reacts with hydrogen fluoride. As the particle size is decreased, some of the metallic particles become entrained in the off-gas stream and deposited in the off-gas system. The remaining particles are found dispersed through the salt melt or adhering to the structural metals of the dissolver. In the latter case they may protect the base metal against corrosion, but they increase the difficulty of inspecting and measuring corrosion losses.⁵

Additional hydrofluorination studies in copper-lined equipment indicated a small effect of temperature and a nonlinear decrease in dissolution rate with increasing concentration of zirconium tetrafluoride in the molten salt.⁵ An important factor in dissolution rate as well as vessel corrosion is gas velocity.

Marked differences found in the corrosivity of various fluoride melts toward structural metals have been attributed to the influence of solvent composition on chemical activities, even when the oxidation-reduction reaction responsible for the corrosion is nominally the same. In order to study this type of thermodynamic system, measurements were made on the heterogeneous equilibrium

$$K = \frac{a_{M^0} P_{HF}^2}{a_{MF_2} P_{H_2}}$$

for the reaction



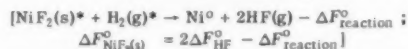
Specifically, tests were made of the reduction by hydrogen of nickel fluoride, ferrous fluoride,

or chromous fluoride dissolved in fused salt. These metals are important constituents in high-nickel alloys such as INOR-8 and Inconel, in stainless steels, and also in Zircaloys. From the processing standpoint, behavior of these elements is important in vessel corrosion and also in the dissolution of fuel elements.

In sodium fluoride-zirconium fluoride salt at 600°C, experimental determinations of the equilibrium constant for the reaction of nickel with hydrogen fluoride give values about 500 times larger than those calculated from previous data. The new data show correspondingly lower equilibrium concentrations of nickel fluoride. The new higher value of the equilibrium constant for nickel relative to chromium and iron provides confirmation of practical effects observed such as the preferential corrosion of chromium from nickel-chromium alloys and the preferential deposition of metallic nickel (by hydrogen or zirconium) from salts containing the fluorides of these elements.

One result of this continuing study is the determination of a revised value of the standard free energy of formation of nickel fluoride.^{29,33} These results are shown in Table IV-6.

Table IV-6 REVISED STANDARD FREE ENERGY OF FORMATION FOR $NiF_2(s)$ ³³



Temp., °C	$2\Delta F_{HF}^0$	$\Delta F_{reaction}^0$	$\Delta F_{NiF_2(s)}^0$	Former $\Delta F_{NiF_2(s)}^0$
600	-131.34	-8.68	-123	-127.88
550	-131.22	-6.73	-124	-129.43
500	-131.12	-4.70	-126	-131.02

*s and g refer to crystalline solid and gaseous states, respectively.

In operation of fused-salt processes, it is desirable to identify compounds and ascertain compositions of many molten-salt mixtures. Accordingly, physical and chemical data are being gathered to aid in analysis of such mixtures. Spectra have been obtained at ORNL³⁴ for nickel fluoride, cobalt fluoride, chromic fluoride, praseodymium fluoride, uranium tetrafluoride, and uranyl fluoride dissolved in molten lithium fluoride-sodium fluoride-potassium fluoride at temperatures ranging from 500 to approximately 650°C. These spectra are compared to similar spectra obtained in other molten salts and aqueous solutions. General

procedures are described which were used in preparing the fluoride salt melt and in recording the spectra by means of a high-temperature cell assembly designed for use with a Cary recording spectrophotometer.³⁴

Structural aspects of molten salts which are of current interest among both theoretical and experimental research workers are discussed in a report from Rensselaer Polytechnic Institute.³⁵ Models for molten salts based on liquid-state theories and on electrochemical properties of these systems are considered. Experimental methods and current problems in the fields of pure molten salts and mixtures are also surveyed.

A comparison of Russian and ORNL investigations of the sodium fluoride-thorium fluoride system has been made at ORNL.³⁶ The preparation of uranium trifluoride and its stability in molten fluorides are discussed. The solubilities of noble gases and hydrogen fluoride in molten salt (NaF-ZrF_4) were found to obey Henry's law. These data are given in Table IV-7.

Table IV-7 SOLUBILITIES OF NOBLE GASES AND HYDROGEN FLUORIDE IN MOLTEN ZIRCONIUM TETRAFLUORIDE-SODIUM FLUORIDE³⁶

(53-47 Mole Ratio NaF-ZrF_4)

Gas	$K = \text{Henry's Law Constant} \times 10^{-3}$		
	600°C	700°C	800°C
Helium	21.6	29.2	42.0
Neon	11.3	18.4	24.7
Argon	5.06	8.07	12.0
Xenon	1.9	3.6	6.3
Hydrogen fluoride	0.75	0.65	0.52

In connection with fused-salt processes, phase relations in molten-salt mixtures are being investigated at ORNL.³⁷ The solubilities of the trifluorides of cerium, lanthanum, samarium, and yttrium were determined in a sodium fluoride-uranium tetrafluoride-zirconium tetrafluoride solvent of composition 50-4-46 mole %, respectively, at 550 to 850°C. The solubility of ceric fluoride in sodium fluoride-zirconium fluoride solvents of varying composition was also determined. Inasmuch as the three rare earths samarium, europium, and gadolinium account for significantly more than half of the poisoning of nuclear reactor fuel by nongaseous elements, rare-earth extraction by a solid solvent might serve as a poison-deple-

tion process. Such a process was demonstrated³⁷ on a laboratory scale employing the reaction



where s = solid, d = dissolved, and ss = solid solution.

Fluorination Processes

A direct fluorination process under study at ANL for the processing of irradiated fuels is based on the conversion of uranium and plutonium to hexafluorides by direct reaction with fluorine gas. Current application of this process is toward recovery of uranium and plutonium from Zircaloy or stainless-steel-clad ceramic fuels and zirconium-based alloy fuels. Fluidization techniques are being used in these gas-solid reaction processes to control the temperature and to remove the heat generated in the reactions.²⁸

A proposed processing procedure utilizes the reaction of zirconium with a mixture of hydrogen fluoride and hydrogen chloride for decladding. Plutonium and uranium hexafluorides, which result from the reaction of the oxide fuel with fluorine, may be separated using a combination of the variability of the rates of fluorination and chemical reactivity. Equipment has been constructed and is being tested to study the process steps using multigram amounts (10 to 100 g) of plutonium.²⁸

A study of the kinetics and mechanism of the decomposition of plutonium hexafluoride vapor has been initiated. Preliminary results²⁸ indicate the reaction to be a heterogeneous one at 160°C. The reaction of plutonium hexafluoride with sulfur tetrafluoride was investigated. Results indicate that plutonium hexafluoride is reduced to nonvolatile plutonium tetrafluoride by sulfur tetrafluoride at rates suitable for process use (99 per cent reacted in 1.5 hr at 70°C) in the separation of plutonium hexafluoride from uranium hexafluoride.

Studies made at ANL indicate that the reaction of sulfur tetrafluoride with uranium trioxide to produce uranium hexafluoride may be used as a basis for a fuel recovery process. Thionyl fluoride and uranium hexafluoride are the major products. In order to use this unique property of sulfur tetrafluoride, it is necessary to find a practical method for the conversion of uranium dioxide to uranium trioxide. Conver-

sion of uranium dioxide to uranium trioxide with air and nitric acid vapor and also with oxygen and nitrogen dioxide was investigated between 350 and 500°C. Excellent results were obtained with nitric acid. However, when using nitrogen dioxide and oxygen, it was apparent that long reaction times and high gaseous pressures were needed for complete conversion of uranium dioxide to uranium trioxide.²⁸

The recovery of uranium from highly enriched uranium-zirconium alloy fuels by reactions with fluorinating gases is under study. One scheme is to convert the metallic element to fluoride salts using mixtures of hydrogen chloride and hydrogen fluoride gases. A subsequent fluorination step would be expected to volatilize the uranium and permit separation. The work is being carried out with the fuel elements submerged in a fluidized bed of inert material (such as calcium fluoride) which serves as the heat-transfer medium. A significant discovery, made at ANL, is that zirconium and Zircaloy can be made to react rapidly with hydrogen fluoride gas by the addition of hydrogen chloride as a catalyst. Laboratory data have been obtained on reaction rates of zirconium with various mixtures of hydrogen fluoride and hydrogen chloride at various temperatures. The data show that the reaction rate increases rapidly up to 10 vol.% hydrogen chloride and then drops off rapidly until the concentration nears 100 per cent hydrogen chloride, at which concentration the reaction rate again increases rapidly. Runs in both 1½- and 6-in.-diameter columns confirmed laboratory results that high rates of conversion of zirconium to the tetrafluoride may be achieved with dilute mixtures of hydrogen chloride in hydrogen fluoride (10 vol.% or less hydrogen chloride) at temperatures of 450 to 500°C. Zirconium tetrafluoride has the advantage of being less volatile and hence easier to handle than zirconium tetrachloride. About 95 per cent conversion was achieved on a 2-kg, 10-plate welded section of a 1.5 per cent uranium-zirconium alloy sub-assembly in about 12 hr. Mixtures rich in hydrogen chloride (nearly 40 vol.%) were found to react less rapidly with zirconium.²⁸

Experiments incorporating a two-zone reaction scheme for reacting zirconium with hydrogen chloride and hydrogen fluoride gases were also initiated. The fuel element is first reacted with hydrogen chloride in the lower part of the fluidized bed to form the volatile zirconium

tetrachloride, which is then reacted in the upper section of the bed with hydrogen fluoride. The two-zone process produces less caking, avoids the production of fines, and gives a fluidizable product. Very little conversion was achieved in the initial trials as a result of back-mixing of the hydrogen fluoride which produced a much less reactive hydrogen chloride-rich mixture. Baffling between the two reaction zones will be required to prevent gas back-mixing.²⁸

The conversion of uranium hexafluoride to uranium dioxide by direct reaction with steam and hydrogen is being investigated as a means for lowering the cost of producing reactor-grade oxide for ceramic fuels. The process involves the formation of either uranyl fluoride or uranium tetrafluoride followed by hydrogen reduction or steam pyrohydrolysis to the dioxide. In each case the newly formed material is deposited as a dense coating on the fluidized particles in the bed. The reaction of steam with uranium hexafluoride was carried out in a fluidized-bed reactor at temperatures of 140 to 230°C using hexafluoride rates equivalent to 205 lb of uranium per hour per square foot of reactor cross section. In the conversion of uranyl fluoride to uranium dioxide, the temperature of the hydrogen reduction step significantly affects the rate of fluoride removal. In 4-hr batch runs, 5 to 10 per cent residual fluoride remained at 550°C and only 0.024 per cent remained at 650°C. The latter value is within the fluoride specification usually set for ceramic-grade uranium dioxide powders. The reduction of uranium hexafluoride with hydrogen to a dense uranium tetrafluoride was successfully carried out in a fluidized bed in a 2.2-hr run at 600°C using a feed rate of 101 g/min and about 250 per cent excess hydrogen. The first series of pellet fabrication studies on uranium dioxide prepared by direct conversion from hexafluoride resulted in sintered densities ranging from 93.5 to 97.5 per cent of theoretical for material which was ground to -325 mesh and pelleted.²⁸

Pyrometallurgical Processes

Melt Refining

The melt-refining process is to be employed for processing the enriched fuel discharged from Argonne's Experimental Breeder Reactor No. 2 (EBR-II). Considerable purification is

accomplished by melting the fuel in a zirconia crucible and holding it at an elevated temperature (1400°C) for several hours. The processing plant located adjacent to the reactor is now under construction at the National Reactor Testing Station (NRTS) in Idaho. This plant also provides for refabrication and reassembly of the fuel for return to the reactor in order to demonstrate a complete fuel cycle, and also to demonstrate any cumulative effects of direct and repetitive fuel recycles. A record of progress in the construction and the development of specialized equipment for the plant is given in quarterly reports^{28,38} of the ANL Chemical Engineering Division, the latest being ANL-6231.

Development of the melt-refining process at Argonne has advanced to a series of demonstration runs employing highly irradiated material (up to at least 1 per cent burnup—10,000 Mwd per ton of fuel). These runs are being performed in Argonne's recently completed high-level gamma facility. The first such run employing a 388-g charge of material having a burnup of 0.6 per cent has now been completed.³⁸ The material was melt refined at 1400°C for 3 hr and was poured into a mold, with a yield of 72 per cent. High yields of 90 per cent or over have not been obtained for this small scale of operation; nevertheless, the yield is slightly low in comparison with an expected yield of around 80 per cent, although the yield obtained is regarded as satisfactory for the first attempt.

Analyses of charge, purified ingot, and the material remaining in the crucible (which was oxidized to a powder in order to obtain representative samples) confirm, in general, previous results obtained with synthetic, highly irradiated, or radioactively spiked alloys. The fission-product removals realized are given in Table IV-8. Removals of greater than 99 per cent were effected for the rare earths and barium, strontium, and iodine. Ninety-five per cent of the tellurium was also removed. Noble metals (exemplified by ruthenium, molybdenum, and zirconium) are not removed by this process. A 9 per cent removal of zirconium is attributed to the presence of carbon in the starting material (~400 ppm).

Knowledge of the nature of the evolution of the noble gases, xenon and krypton, during melt refining is important process information. For example, a rapid evolution of these gases at the melting point would be undesirable. The course

Table IV-8 FISSION-PRODUCT REMOVALS EFFECTED IN HIGH-ACTIVITY-LEVEL DEMONSTRATION OF THE MELT-REFINING PROCESS³⁸

(Starting Material: 388 g of 5 Per Cent Fissium* Pins, 10 Per Cent Enriched in U²³⁵ Irradiated to 0.6 Per Cent Burnup; Process Conditions: Liquefaction for 3 Hr at 1400°C in a Zirconia Crucible)

Element	Per cent removed
Rare earths plus yttrium	99.4
Barium and strontium	> 99.9
Cesium	> 99
Tellurium	95.4
Iodine	> 99.9
Zirconium	9.2
Ruthenium and molybdenum	0

* The composition of the fissium employed was as follows (concentrations in weight per cent): zirconium, 0.118; molybdenum, 2.59; ruthenium, 2.11; palladium, 0.186; rhodium, 0.26; and niobium, 0.01.

of xenon and krypton evolution during heating was followed for a fuel pin similar to one of those used in the melt-refining experiments described above (1.5 in. long by 0.143 in. in diameter—the same diameter as that of an EBR-II fuel pin). The material had been cooled for 49 days prior to the experiment. The patterns of xenon and krypton evolution were the same (see Fig. 6). At a heating rate of 5°C per minute, evolution began at a temperature of about 700°C, was fairly rapid at 800°C, and was complete when the temperature had reached 1020°C. At this latter temperature the pin began to lose its cylindrical shape, and at 1080°C melting appeared to be complete. The evolution was accompanied by swelling of the pin, the diameter increasing by about 40 per cent between 700 and 800°C. It appears, therefore, that the evolution of xenon and krypton is gradual, beginning at around 700°C and being complete by the time the melting point has been reached.

In the process cell of the EBR-II facility, the argon atmosphere may contain as much as 5 per cent nitrogen. Since the clad, sodium-coated (for heat-transfer purposes in the reactor) fuel pins are expected to reach a temperature of around 300°C during storage as a result of fission-product decay heat, the probable extent of uranium nitride formation under these conditions has been considered. Laboratory experiments with uranium and uranium-5 per cent fissium alloy pins show that the extent of nitridation is significant under the above con-

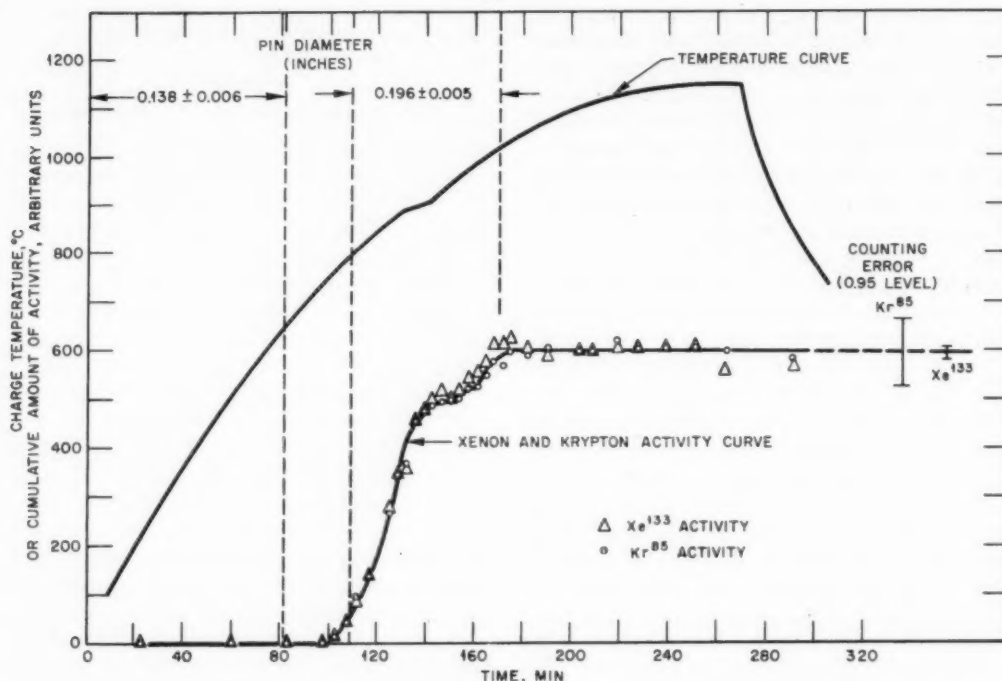


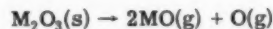
Figure 6—Xenon and krypton evolution from a highly irradiated uranium alloy pin.³⁸ Charge: Uranium -5 per cent fissium pin; length, 1.5 in.; diameter, 0.143 in.; weight, 7.17 g; total atom burnup, ~0.6 per cent; cooling time, 49 days. Atmosphere: high-purity argon; pressure, 685–790 mm (constant volume at STP).

ditions and is increased somewhat by sodium coatings.³⁸ In 17.5 hr at a temperature slightly above 300°C, pins weighing 100 g reacted with the following amounts of nitrogen: uncoated uranium pins, 1.47×10^{-4} mole; sodium-coated uranium pins, 2.48×10^{-4} mole; uncoated uranium-fissium pins, 1.73×10^{-4} mole; and sodium-coated uranium-fissium pins, 3.02×10^{-4} mole of nitrogen.

General and Fundamental Information. The proceedings of an international symposium on high-temperature technology have been issued in book form.³⁹ These proceedings were previously reviewed²⁴ as a collection of "advance papers." A book, *Kinetics of High-Temperature Processes*, by Kingery,⁴⁰ contains information pertinent to the selection of materials and to phenomena encountered in pyrochemical processes, such as those involved in the previously discussed melt-refining process. Of particular interest is material on diffusion of oxygen in oxides. Also germane to this general subject are the proceedings (published in 1959) of the

second national conference on high-temperature chemistry⁴¹ held in Paris in 1957. The published proceedings include information on compounds and solid solutions formed by zirconia with oxides of trivalent and tetravalent metals. Phase equilibria and other thermodynamic information have been reported for various metal oxide and nitride systems, with particular emphasis on the rare-earth metal systems.⁴²

A study of the vaporization of La_2O_3 , Nd_2O_3 , and Y_2O_3 has been reported by Walsh et al.⁴³ When tungsten Knudsen effusion cells were employed, each of the oxides vaporized by the following path:



The dissociation pressures for the above reaction at several temperatures are given in Table IV-9.* With tantalum cells, substantial vaporiza-

*Table IV-9 is adapted from data given⁴³ in the *Journal of the American Ceramic Society*.

Table IV-9 PARTIAL PRESSURES OF RARE-EARTH OXIDES⁴³

[Reaction $M_2O_3(s) \rightarrow 2MO(g) + O(g)$]			
M	Temp., °K	P_{MO} , atm $\times 10^6$	P_{O_2} , atm $\times 10^6$
Lanthanum	2230	4.84	0.78
	2340	13.9	2.23
	2440	55.5	8.90
Neodymium	2250	4.63	0.74
	2300	9.4	1.50
	2400	40.0	6.39
Yttrium	2500	2.70	0.53
	2600	8.63	1.69
	2700	24.0	4.73

tion occurred at temperatures 200 to 300° lower than with tungsten because of the reaction with tantalum to form the gaseous rare-earth monoxide and a gaseous tantalum oxide. Various other measured and derived thermodynamic properties are reported, and some generalizations are made concerning the vaporization behavior of rare-earth oxides. Free-energy functions for gaseous monoxides have been calculated from presently available spectroscopic results.⁴⁴ The results of these calculations have been tabulated for 500° intervals from room temperature up to 3000°K.

Low-temperature (below 1500°C) equilibria between zirconia, thoria, and urania have been discussed by Mumpton and Roy.⁴⁵ A continuous series of solid solutions could be made between thoria and urania at 1300°C. However, only 8 mole % urania dissolves in zirconia, and less than 4 mole % zirconia dissolves in urania at 1300°C. Metastable solid solutions of thoria in zirconia were prepared at temperatures below about 400°C. Above this temperature the solubility of one oxide in the other was low (about 2 mole % up to 1000°C).

Because of difficulty in obtaining various shapes of high-purity magnesia from commercial sources at the time they were needed, the ceramics group at ANL investigated the fabrication of magnesium oxide for use as a container material for the melting and purification of uranium.⁴⁶ The melting point of magnesium oxide was also determined, and various phase studies were performed on the magnesia-uranium system and on the magnesia- U_3O_8 system.

Processing of Ceramic Fuels. Recent reviews^{12,23,47} have included information on the

development of the "salt-cycle" process by which uranium dioxide may be dissolved at 700 to 800°C in a molten-salt solution (sodium chloride-potassium chloride) by reaction with various chlorinating agents to give uranyl chloride and subsequently reduced by appropriate reducing agents or electrolytically to uranium dioxide. This procedure is potentially useful as a process for uranium dioxide fuels. A report summarizing laboratory development of this process has recently been issued.⁴⁸ The report discusses investigations of various chlorinating agents, salt compositions, and reducing agents which led to the general selection of chlorine as the chlorinating agent, an equimolar mixture of sodium chloride-potassium chloride as the salt, and electrolytic reduction as the reduction procedure.

This preliminary work culminated in the preparation of a total of 5 kg of uranium dioxide by electrolytic reduction in a 2-liter fused silica vessel. Uranium trioxide was generally used for the preparation of the uranyl chloride solution. X-ray diffraction patterns of the uranium dioxide product, which had a tap density of 6.2 g/cm³, showed a typical cubic uranium dioxide structure and no evidence of any other oxide impurity. Figure 7 is a picture of a typical uranium dioxide product deposited on a graphite cathode.

The above report⁴⁸ also points out that plutonium and thorium oxides do not behave in the same manner as uranium oxides. Plutonium and thorium oxides may not dissolve at all, or may dissolve extremely slowly, under conditions used for uranium dioxide dissolution, although plutonium dioxide will react with anhydrous hydrogen chloride or aluminum chloride to yield plutonium trichloride. By utilizing this difference in behavior of thorium, plutonium, and uranium oxides, uranium oxides may be selectively removed from oxide mixtures. A separation factor of 58 from plutonium dioxide was realized in one experiment and of 500 from thorium oxide in another experiment. It is believed that uranium can similarly be separated from oxides of other actinide elements. The electrolysis of uranyl chloride in a potassium chloride-lithium chloride eutectic at 450°C was also studied by Hill and Osteryoung.⁴⁹ They found the standard potential on a mole fraction scale for the $UO_2(II)-UO_2(0)$ couple to be -0.286 volt against a standard Pt(II)-Pt(0) reference electrode.

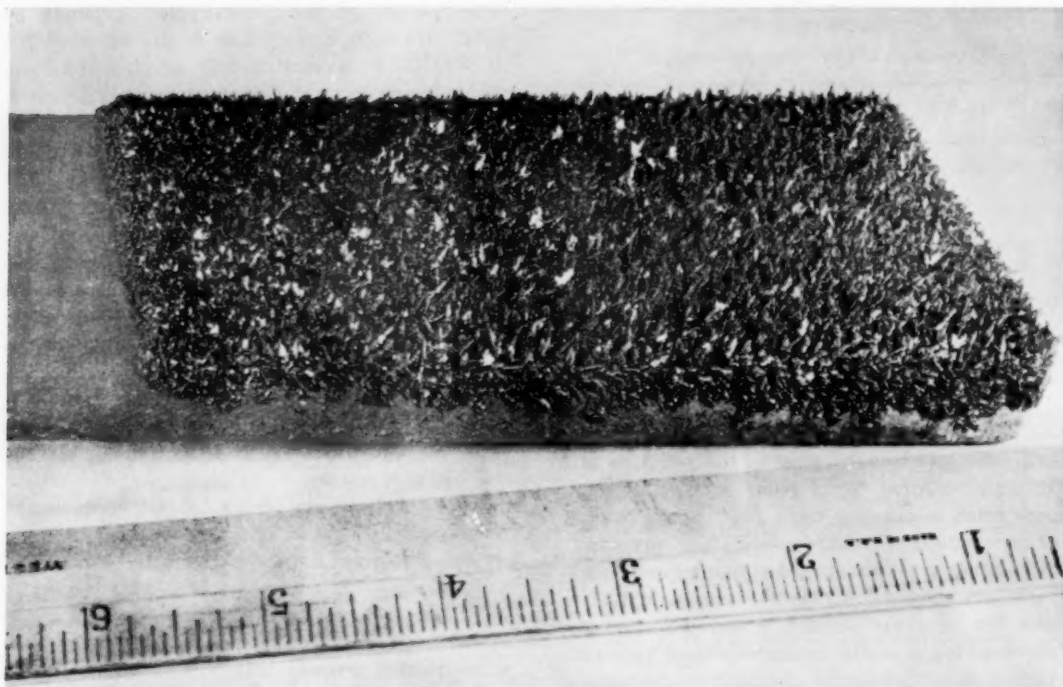


Figure 7—Typical uranium dioxide product deposited on a graphite cathode.⁴⁸

The latest progress reports from Hanford²⁰⁻²² have dealt generally with scaleup of the salt-cycle process, with new developments in process chemistry, and with investigation of container materials. A 20-liter electrolytic cell has been constructed and is being operated for production of 5- to 10-lb lots of uranium dioxide. Over 45 lb of electrolytic uranium dioxide has been produced by electrolysis at 710°C. By continual improvement of conditions, the oxygen-uranium ratio of the product has been reduced to 2.01 and sometimes lower.²² Over 90 per cent of the uranium has been removed at current efficiencies of 80 per cent.²¹ Construction of a hot cell for radioactive demonstration of the salt-cycle process is essentially complete, and cold runs have been started.²²

In conceptual salt-cycle flow sheets, repetitive use of sodium chloride-potassium chloride salt is planned. Equilibrium fission-product concentrations would be maintained by discarding a fraction of the salt after each cycle. An alternative procedure would be to scavenge fission products from the molten salt. Initial experiments have shown removal of about 95

per cent of tracer Ru^{106} by the addition of less than 1 per cent zinc sulfide to the melt.²⁰ It is believed that a variety of chemical compounds, oxides and sulfides, may be useful for this purpose. Rare-earth compounds in the salt phase are precipitated by exposure to air; the precipitate is suspected to be an oxychloride.²²

Alternate chloride systems are being investigated in the hope of reducing the temperature of operation and thereby the corrosive attack on various materials. Chlorides of zinc, mercury (mercuric), cadmium, and lead employed separately in combination with potassium chloride all gave low rates of dissolution of uranium dioxide under the action of chlorine (0.2 to 1.2 g/hr as compared to 9 g/hr for the sodium chloride-potassium chloride system).²¹

As implied above, one of the major problems of the salt-cycle process is the selection of container materials that resist corrosion. The resistance of various container materials to corrosion is discussed on page 40 of this issue.

Preliminary development of a somewhat complicated method of processing high-fired uranium dioxide fuels by a reduction-mercury

extraction-steam oxidation process has recently been reported.⁵⁰ This is an adaptation of the Hermex⁵¹ process under development at ORNL, in which mercury is used as a liquid-metal solvent for uranium. Uranium dioxide (pellets and powder fired at 1750°C) has been reduced at 1000°C by magnesium in the presence of a magnesium chloride flux, with yields to date as high as 93 per cent. The uranium product was stated to be nonpyrophoric and in the form of spheres having diameters of 0.5 to 50 μ . The uranium was then dissolved in boiling mercury; the resulting solution was filtered hot to remove insoluble material and was then cooled and filtered again at 25°C to isolate uranium mercuride. For purification purposes, the uranium was again dissolved in mercury, and the mercuride was again crystallized and isolated by filtration. The uranium mercuride was then decomposed by steam at 200°C which converted the uranium to an oxide. A wash with boiling mercury served to remove noble metals. The uranium oxide concentrate was then re-torted at 900°C to provide removal of the mercury.

The oxide product had an oxygen-uranium ratio of 2.43, which must be reduced. A re-constituted pellet of processed oxide had a density of 9.76, 89 per cent of theoretical. Inactive ruthenium, cesium, and samarium, added in amounts equivalent to concentrations expected for burnup of 30,000 Mwd per ton of fuel, were decontaminated by factors of $>10^3$, 220, and 75, respectively.

Atomics International is investigating a process for recycle of uranium oxide fuels which is based on alternate high-temperature air oxidation and hydrogen reduction cycles to comminute the fuel. Although some decontamination is realized, the primary goal is reenrichment and refabrication of fuel shapes. Multicycle processing and refabrication experiments have been carried out on a uranium oxide fuel with the addition of 2 per cent fission-product oxides before the start of each cycle to simulate fuel after burnup in a reactor.⁵² This material was carried through five cycles to a final fission-product oxide concentration of 10 per cent fission-product oxides. It appears from this work that high-burnup uranium oxide fuels can be processed and re-formed into new bodies for return to the reactor. The presence of fission-product oxides had no deleterious effect on the sinterability of the oxide mixture (if

anything, it had a slight enhancing effect) since densities approaching 98 per cent of the theoretical were obtained at the higher concentrations of fission oxide.

Process studies for uranium carbide fuels are also continuing at Atomics International. These studies generally involve low-temperature conversion of uranium carbide to uranium dioxide and a high-temperature reconversion to carbide in the presence of excess carbon, or the chlorination of uranium carbide and a subsequent reaction to give the carbide. Experimentation is in a preliminary stage.

Liquid Metal and Salt Processes

Liquid metal and salt systems are being investigated at several sites as processing media in which to effect the reactions and separations necessary for the purification of discharged reactor-fuel materials. The processes generally consist of dissolution in an appropriate liquid-metal system, purification of the desired elements by crystallization procedures or by extractions with immiscible molten salts or other liquid metals, and, finally, recovery of the desired elements as metal by evaporation of the solvent. A patent for such a process in zinc media has recently been granted.⁵³

The solubilities of the elements whose separations are being attempted are of prime importance in the design of processing schemes. The solubilities of various elements in liquid cadmium have been recently determined and are represented by the following equations:³⁸

$$\log \text{ at. \% Ti (325 to 650}^\circ\text{C)} \\ = 3.237 - 5333T^{-1} + 1.468 \times 10^5 T^{-2}$$

$$\log \text{ wt. \% Zr (325 to 452}^\circ\text{C)} = 3.058 - 2750T^{-1}$$

$$\log \text{ wt. \% Zr (452 to 575}^\circ\text{C)} = 1.079 - 1314T^{-1}$$

$$\log \text{ wt. \% Sm (325 to 420}^\circ\text{C)} = 7.0729 - 4878.2T^{-1}$$

$$\log \text{ at. \% Sm (420 to 609}^\circ\text{C)} = 3.0911 - 2116.17^{-1}$$

$$\log \text{ wt. \% Y (325 to 600}^\circ\text{C)} \\ = 4.8539 - 4687.5T^{-1} + 0.7520 \times 10^6 T^{-2}$$

The solubilities of various elements in liquid mercury, in the range from room temperature to 356°C, have been reported as follows:⁵⁴

$$\log \text{ wt. \% U} = 2.33213 - 1418.83T^{-1}$$

$$\log \text{ wt. \% Th} = 0.426493 - 698.472T^{-1}$$

$$\log \text{ wt. \% Gd} = 1.83770 - 1221.01T^{-1}$$

$$\log \text{wt.}\% \text{ Sm} = 1.41450 - 1036.45T^{-1}$$

$$\log \text{wt.}\% \text{ Nd} = 1.65023 - 1163.16T^{-1}$$

In mercury saturated with uranium, the solubilities of zirconium and molybdenum over the same temperature range (25 to 356°C) were below the limit of analytical detection ($<4 \times 10^{-4}$ and $<5 \times 10^{-5}$ wt.%, respectively). Ruthenium and palladium solubilities were also determined in uranium-saturated mercury and were very low, ruthenium's solubility ranging from 0.002 to 0.01 wt.% and palladium's from 0.00004 to 0.00002 wt.%.

Pertinent thermodynamic data for solute elements in liquid-metal systems are being determined at ANL,³⁸ Ames Laboratory,⁵⁵⁻⁵⁷ and ORNL.^{5,54} These include the nature of the solid phase in equilibrium with the liquid, the free energy of formation of intermetallic compounds, and the activity coefficients of solute elements. Results of thermal analyses and metallographic data for the yttrium-zinc system have been summarized in a phase diagram for this system (Fig. 8).⁵⁵ Seven intermetallic compounds are shown, and the possibility of another is indicated. A phase diagram for the uranium-

mercury system based on vapor pressure data for the temperature range from 25 to 431°C has been reported.⁵

Of considerable significance in the design of liquid metal and salt processes is the ability to oxidize and reduce elements or compounds in order to control their distribution between liquid metal and a solid phase or a molten-salt phase. At Argonne, a process for recovery of fissionable material in the residue (or skull) remaining in the zirconia crucible after a melt-refining operation is based on the ability to reduce uranium oxides by magnesium dissolved in zinc. Oxidation of the skull material in the crucible is necessary to convert it to a free-flowing powder which may be poured essentially quantitatively from the crucible.³⁸ Essentially quantitative reductions of skull oxides (uranium present principally as U_3O_8) and of uranium dioxide have been achieved in times of less than 8 hr at 800°C in a dilute magnesium (10 per cent)-zinc solution and also in pure magnesium containing a small amount of sodium (0.5 to 2 per cent) as a wetting agent.³⁸ Extensive reduction (58, 78, and 93 per cent) of 1750°C-fired uranium dioxide powder and pellets at 1000°C by magnesium in the presence of anhydrous magnesium chloride as a flux has been reported⁴⁹ (see also page 35 of this issue).

At Ames Laboratory, selective oxidation-reduction reactions are being employed to effect a desirable distribution of elements between a molten potassium chloride-lithium chloride eutectic salt phase and a molten zinc phase. Zinc chloride has been used as the oxidant; magnesium as the reductant. The reactions involved in transfer of various solute elements between the salt and metal phases have been identified, and equilibrium constants have been determined.⁵⁷ These enable an evaluation of the distribution coefficient between the phases. In general, many metals may be separated from uranium by the oxidation-reduction procedure. However, in the particular salt-metal system employed, the separation of thorium and yttrium from uranium does not appear to be particularly favorable.

The possibility of employing immiscible or slightly immiscible liquid-metal systems to effect separations is being explored at Argonne and Ames. The distribution coefficient of a number of representative fissile and fission-product elements between the two immiscible liquids, lead and zinc, at about 735°C has been

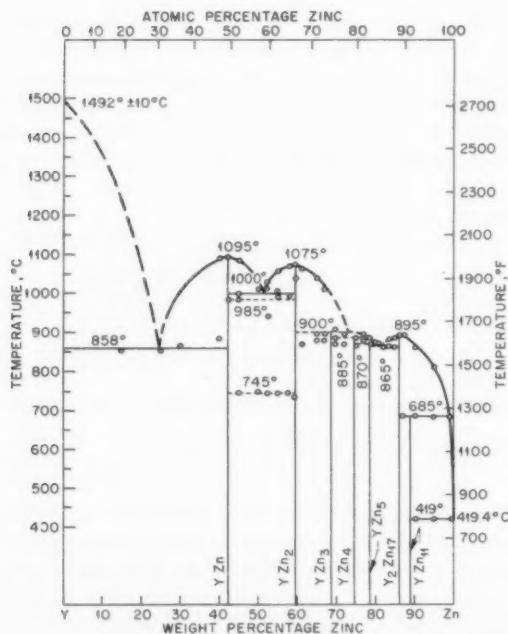


Figure 8—Phase diagram for the yttrium-zinc system.⁵⁵

measured.³⁸ Values of the coefficient (weight per cent in zinc phase/weight per cent in lead phase) are: uranium, 31.9; palladium, 150; cerium, 3.7; and strontium, 0.14. The coefficient for uranium was found to vary from 31.9 at 734°C to 270 at 647°C.

At Ames, use of a magnesium-silver eutectic metal solution for extraction of irradiated uranium-chromium eutectic samples (temperature of approximately 1000°C) has been studied.⁵⁵⁻⁵⁷ Distribution coefficients in favor of the magnesium-silver phase were fairly high for barium, strontium, cesium, cerium, yttrium, lanthanum, and tellurium. Ruthenium, zirconium, and niobium were poorly extracted, although 50 to 60 per cent of the zirconium was removed from the system, probably through a carbide slagging mechanism. The distribution coefficient for plutonium was also rather low, only about 25 per cent being removed in a single extraction. Nearly equal volumes of the two alloys were used.

Fundamental Studies. The electrochemical behavior of uranium in fused salts has been the subject of a recent study by Hill and Osteryoung.⁴⁹ Two eutectic chloride salts were chosen for the study: a binary lithium chloride (59 mole %)-potassium chloride (41 mole %), and a ternary magnesium chloride (50 mole %)-sodium chloride (30 mole %)-potassium chloride (20 mole %). The first salt has been used in many other electrochemical investigations and affords direct comparisons of uranium electrode potentials with those of other metals. The latter salt was used because of its application in the fission-product extraction process proposed for the Liquid Metal Fuel Reactor (LMFR).

The polarographic and potentiometric behavior of various uranium species in the above salts were studied. Measured cell potentials are given in Table IV-10. Implications concerning various reactions in the salt phase are discussed.

Corrosion

Many of the processes under development for present and future fuels involve unusually corrosive reagents. In order to assist in the selection of construction materials for these processes, extensive corrosion programs have been initiated. Results reported under this

Table IV-10 COMPARISON OF MEASURED CELL POTENTIALS WITH THOSE CALCULATED FROM THERMODYNAMIC DATA* FOR THE PURE COMPOUNDS⁴⁹ AT 450°C

Cell	Solvent eutectic†	Potential measured, volts	Potential calculated, volts
U U(III) Ag(I) Ag	Binary	-1.61	-1.619
U U(III) Ag(I) Ag	Ternary	-1.61	-1.619
Ag Ag(I) Pt(II) Pt	Binary	-0.637*	-0.612
U U(III) Pt(II) Pt	Binary	-2.25	-2.231
U U(III) Pt(II) Pt	Ternary	-2.25	-2.231
Pt U(IV)U(III) Pt(II) Pt	Binary	-1.25	-0.835
Pt U(IV)U(III) Pt(II) Pt	Ternary	-1.30	-0.835
U U(IV) Pt(II) Pt	Binary	-2.00*	-1.882
U U(IV) Pt(II) Pt	Ternary	-2.01	-1.882

* Obtained from other authors as indicated in original article.

† Binary refers to a 59 mole % LiCl-41 mole % KCl eutectic; ternary refers to a 50 mole % MgCl₂-30 mole % NaCl-20 mole % KCl eutectic.

heading are, in general, restricted to those areas of development in which separate corrosion programs have been established. Where no specific programs exist, data are usually reported in the section of this review related to those processes.

Solvent Extraction

The present AEC production plants for fuel processing are of the solvent-extraction type. Many of the newer fuels, particularly those associated with the power-reactor demonstration program, cannot be processed directly in these plants. Several AEC contractors have under development so-called head-end procedures to pretreat such fuels in order to produce feeds that are compatible with the existing plants.

One such fuel requiring a head-end treatment is that from the Consolidated Edison reactor at Indian Point, N. Y. The fuel is stainless-steel-clad uranium oxide-thorium oxide. Two combinations of processing procedures are available for these fuels: Darex-Thorex and Sulfex-Thorex. In the first, decladding is accomplished with a nitric acid-hydrochloric acid mixture, and in the second, with 4M to 6M sulfuric acid. Dissolution of the fuel in each case is accomplished with nitric acid containing some fluoride ion. The most promising construction materials are titanium for nitric acid-hydrochloric acid and Nionel for sulfuric acid.

The resistance of titanium to the Darex de-cladding portion of the cycle has been demonstrated. Tests are continuing on its resistance to Thorex and Thorex-feed-adjustment solutions.^{5,58} In boil-down tests of thorium-uranium fuel solutions prepared with the dissolvent (13M nitric acid-0.04M sodium fluoride-0.004M iron-100 ppm chloride), titanium corrosion was serious near the bottom of the condenser at total reflux. In laboratory tests in which titanium was exposed to the initial feed-adjustment solutions, the instantaneous corrosion rate at the bottom of the condenser was low initially, increasing with time to a rate of 1.3 mils/month at 840 hr (corresponding to 0.7 mil/month average rate over this period).⁵⁸ However, during 35 actual boil-down cycles covering a period of 130 hr of exposure, the attack was found to be negligible.

There is some concern regarding the possibility of severe corrosion resulting from concentration of fluoride during rectification of vapors from the Thorex boil-down. A series of tests with titanium 45A was made in a number of compositions of nitric acid with 0.005M and 0.05M hydrofluoric acid.^{5,58} Specimens were exposed in the liquid, at the interface, and in the vapor phase. The results are shown in Fig. 9. In the nitric acid concentration range studied, corrosion rates are about a factor of 10 greater with the higher fluoride content (liquid and interface samples only). The maximum rate occurs when the nitric acid concentration is 6M. The corrosion of vapor-phase samples increases with nitric acid concentration. This is probably attributable to the higher vapor pressure of hydrogen fluoride when the concentration of nitric acid in the liquid phase is higher. In similar tests with type 309SNb stainless steel, the maximum rate observed was 56 mils/month in 15M nitric acid-0.05M fluoride ion, and the minimum rate was 1 mil/month in 3M nitric acid-0.005M fluoride ion. If the above data are applied, the maximum corrosion rates to be expected are less than 1 mil/month for titanium 45A at the start of boil-down and 4 mils/month for type 309SNb stainless steel during the period when the condensate is 13.5M nitric acid and a maximum of 0.0017M fluoride ion.

Corrosion rate of Nionel in the Sulfex de-cladding portion of the Sulfex-Thorex process is 5.3 mils/month (4M sulfuric acid).⁵ With this beginning acid concentration, it has been found difficult to overcome the natural passivation of

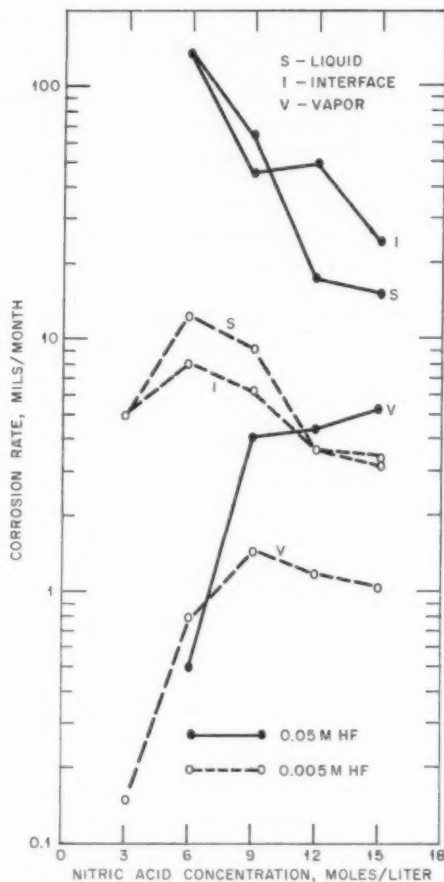


Figure 9—Corrosion rates of titanium 45A in nitric acid-hydrofluoric acid mixtures.^{5,58}

the cladding to be dissolved. Initial concentrations of 8M, 10M, or 12M were found to overcome this passivity, and dissolution proceeded normally at the subsequently reduced 4M concentration. The maximum observable corrosion rates for the three higher concentrations were 4, 9, and 130 mils/month, respectively. The first two values were considered reasonable for the process, particularly in view of the fact that contact with the higher concentration acid would be brief; 12M acid was rejected.

The general corrosion of Nionel in Thorex dissolver solutions has been found to be satisfactory; however, localized effects in the vicinity of welds have been found to be serious. A laboratory dissolver used for 25 Sulfex-Thorex cycles showed an over-all corrosion rate of 2.9 mils/month, but localized attack around

welds was considerably more severe. Proper heat-treatment corrects this.⁵ All test samples heated to temperatures between 1500 and 1800°F showed some signs of localized corrosion in the heat-affected zone. Welds annealed for 1 to 2 hr at 1850 to 1950°F and quenched showed the least corrosion.

It was reported in the October 1960 issue of *Reactor Fuel Processing* that the ICPP is interested in modifying its solvent-extraction procedure for zirconium-matrix fuels to adapt it for use with higher uranium content fuels. ICPP states that the existing process for high zirconium-uranium fuels has the following major disadvantages: (1) high waste volumes, (2) restriction to 1½ per cent or lower uranium alloys by solubility, (3) inability to handle oxide fuels, and (4) the liberation of hydrogen in the off-gas.⁵⁹ In order to study process modifications in a scaled-up facility, ICPP has constructed a pilot plant in which the major construction material is annealed Carpenter-20 alloy. Exceptions are vessels and process piping that do not come into contact with hydrofluoric acid. These were constructed of stainless steel.⁶⁰ Carpenter-20 was selected as the best compromise alloy for service with the nitric acid-hydrofluoric acid mixtures. Although intended for zirconium-matrix fuels, the initial testing of the pilot plant was done with an aluminum dissolution flow sheet.⁵⁹ A second step of the plant startup was made with a fuel composition of 2 per cent zirconium-98 per cent uranium. This was done since only small quantities of hydrofluoric acid are required and the acid is complexed with aluminum nitrate in the feed. During these tests a canned rotor feed pump became inoperative, and subsequent analysis indicated that deposits which caused the freeze were attributable to dissolution products of Carpenter-20. Several cracks and leaks have occurred in and around the welds between wrought Carpenter-20 pipe and cast Carpenter-20 fittings. The majority of these leaks have been found adjacent to the welds in the cast material.

With the advent of many new fuel compositions, it has become increasingly difficult to apply to them the dissolution chemistry of existing processes. Need for a universal head-end process is continually becoming more acute.⁵⁹ Scoping studies at the ICPP have shown the electrolytic dissolution method to come as close to handling all fuels as any single method. The

electrical potential overcomes the passivity of stainless steel in nitric acid solutions. Zirconium metal shows partial solubility and partial hydrolysis to solid hydrates in aqueous systems. It may be possible to process metallic-clad uranium oxide fuels by decladding electrolytically and dissolving the oxide chemically.⁶⁰ The selection of construction materials for an electrolytic system involves factors other than those usually considered. Promising materials for use as anode connectors to the dissolving fuel are tantalum and niobium and alloys of these metals with tungsten.⁶⁰ The principal problem associated with these alloys is the increase of contact resistance with time. The use of noble metals overcomes this problem but at the expense of decreased efficiency resulting from an oxygen evolution reaction.

The electrolytic dissolver vessel itself might logically be used as the cathode. A number of materials were tested in three nitric acid concentrations at two temperatures with cathodic current densities⁶⁰ of 1 amp/cm². The results are shown in Table IV-11. The largest cor-

Table IV-11 CORROSION RATES OF POSSIBLE CATHODE MATERIALS FOR ELECTROLYTIC DISSOLUTION OF STAINLESS STEEL IN NITRIC ACID⁶⁰

(Current Density: 1 amp/cm²)

Materials	HNO ₃ conc.	Temp.	Corrosion, mils/month
Carpenter-20	4M	20°C	130
Carpenter-20	35%	Boiling	Nil
Carpenter-20	70%	Boiling	Nil
S.S.-347	4M	20°C	200
S.S.-347	35%	Boiling	Nil
S.S.-347	70%	Boiling	Nil
Niobium	4M	20°C	Nil
Niobium	35%	Boiling	Nil
Titanium	4M	20°C	1.4
Titanium	35%	Boiling	Nil
Nionel	4M	20°C	140
Inconel	4M	20°C	140
Zirconium	4M	20°C	Nil
Chromium	4M	20°C	Nil
Tantalum	4M	20°C	Nil

rosion rates were observed in room-temperature exposures. Carpenter-20 and stainless-steel type 347 which had corrosion rates of 130 or more mils per month at 20°C (4M acid) corroded at nearly negligible rates under refluxing

conditions with both 35 and 70 per cent acid. Niobium and titanium showed good results at both temperatures.

Fused-Salt and Volatility Processing Methods

A process not previously discussed in the corrosion section of this Review is the ARCO process which is under development at ICPP. This is intended primarily as a head-end process and is specifically directed to zirconium-uranium alloys. The fuel alloy is dissolved in molten lead chloride at an elevated temperature. The zirconium dissolution product is removed as the volatile tetrachloride. The product salt contains the uranium (principally as the trichloride) together with excess lead chloride and the alkali, alkaline earth, and rare-earth fission products. Ruthenium tends to remain in the lead reaction product layer. Uranium salts are quantitatively leached from the lead chloride product matrix with 8M nitric acid. Following composition adjustment, this feed would be introduced into the solvent-extraction plant.

A number of nickel-base and stainless-steel alloys were subjected to lead-lead chloride mixtures at 528°C for a period of 18 days.^{59,60} Hastelloy F and Inconel X corroded at rates of about 5 mils/month in the unwelded condition; rates for Hastelloy C, Incoloy 804, and Carpenter-20 were 8 to 11 mils/month. The corrosion rate of the first two alloys decreased with time, whereas that of Carpenter-20 increased.

Hanford has been working on a fused-chloride electrolytic fuel recovery process for U_3O_8 . A corrosion program directed toward developing a metallic container for this process was initiated at BMI under Hanford's direction.

The process consists of chlorinating a uranium oxide (U_3O_8) with chlorine or hydrogen chloride in an equimolar melt of sodium and potassium chloride to form uranyl chloride. In a second step, uranium dioxide is deposited at the cathode by electrolysis of the molten-salt solution. Temperatures are approximately 750 to 800°C. Construction materials to be tested are exposed to the molten chloride melt (containing U_3O_8) through which gaseous chlorine and oxygen are bubbled. This simulates the first process step. To simulate the second process step, the oxygen is omitted. In preliminary experiments nickel and a nickel-base alloy were tested. These were rapidly attacked,

and very extensive local attack occurred at the liquid-vapor interface.⁶¹

Some preliminary corrosion experiments with nonmetallic construction materials were also made at Hanford.²⁰⁻²² Crucibles made of silicon carbide were found to be excessively porous to the melt. Zirconia crucibles were an improvement in so far as no leakage occurred through the crucible until after 48 hr of exposure. Silicon carbide bonded with silicon nitride was found to react rapidly with the salt mixture. In addition, some metallic construction materials have been tested. Nickel- and cobalt-base alloys, austenitic stainless steels, and tantalum were found to have corrosion rates of 100 mils/month and up. Platinum is the best to date at 3 mils/month.²¹

In Table IV-6, on page 34 of the July 1960 issue of *Reactor Fuel Processing*, the values for the corrosion rate of nickel at 50°C in a nitrogen dioxide-hydrofluoric acid environment were reported in units of mils per month. The units should have been $mg/(cm^2)(min)$. The value of 0.016 should have read 0.060. The correct values in mils per month are: 0.64, 0.45, and 1.9.

Pyrometallurgical Processing

Pyrometallurgical processing techniques involve the purification and decontamination of reactor fuels without making a transformation from the metallic state. Oxide slagging of the molten fuel, preferential extraction of constituents in molten metals, or dissolution and crystallization from molten metals are examples of techniques being explored. A number of these processes require operations at temperatures above the melting point of uranium, 1132°C. Corrosion work with molten plutonium and/or its alloys at Los Alamos for application in the LAMPRE-I reactor is considered relevant although the application per se does not involve processing operations. With the advent of a new unclassified series of reports on the part of Los Alamos, it is now possible for the reader to follow the program in greater detail.⁶² In the first unclassified report in the series is a summary of the general status of the LAMPRE program. The present approach to the construction material problem in the LAMPRE-I reactor is to use the very best material known, from the standpoints of corrosion resistance and fabricability, at what is considered a modest

operating temperature of 570°C. A useful life at this temperature in excess of 2000 hr is considered adequate for the reactor experiment.

A summary of their conclusions to date is as follows: (1) fuel alloys made from plutonium and pure iron are much more readily corroded than are alloys made with cast iron; it is thought that the carbon content of the latter is exerting a protective effect; (2) of the two methods of fabricating the capsules, namely, deep drawing and impacting and ironing,* the latter is structurally better and more corrosion resistant; (3) unless annealed after fabrication, high-purity tantalum capsules are useless for the containment of fuel; polishing after annealing appears to be disadvantageous; and (4) the addition of 0.1 per cent tungsten improves the corrosion resistance of tantalum.⁶²

It was reported in the preceding Review that Los Alamos, with the cooperation of BMI, was undertaking an alloy development program in which small additions of a large number of elements were made to tantalum. The addition of 0.1 per cent tungsten to tantalum has been found to be effective in refining the coarse-grain structure normally seen in annealed metal.⁶²

Pyrometallurgical experiments at ANL are being conducted in a variety of molten-metal environments. The environments include zinc and cadmium with or without small quantities of magnesium. A corrosion loop to determine the compatibility of mild steel with cadmium-1 per cent uranium-2 per cent magnesium alloy was operated for a period of 200 days.^{28, 63} An electromagnetic pump circulated the liquid metal at 550°C at a rate of 1 gal/min. Preliminary examination of the loop shows little evidence of internal corrosion. Periodic samples of the circulating alloy indicated that the uranium concentration in solution had remained essentially constant for the last five months at about 0.85 per cent after a rapid initial decrease from 0.94 per cent. In another series of experiments, cadmium solutions containing up to 3 per cent uranium were shown to be

stable in stainless-steel types 405 and 410 at temperatures⁶³ of up to 550°C. At a temperature of 700°C, uranium was removed from cadmium solution presumably by interaction with the steel. When a cadmium-2 per cent magnesium-0.6 per cent uranium solution was held in a graphite crucible at 700°C, the uranium concentration appeared to decrease within 6 hr. The reaction of a cadmium-2 per cent magnesium-0.9 per cent uranium solution (contained in an alumina crucible) at 700°C with a 25 per cent nitrogen-argon atmosphere was found to be negligible over a 12-hr period.

One of the methods proposed for handling zirconium-matrix fuels is the Zircex process. The fuel is first hydrochlorinated at temperatures of 300 to 600°C. The bulk of the zirconium is removed from the system as the volatile zirconium tetrachloride. The uranium-containing residue is chlorinated with carbon tetrachloride vapors, thus converting the uranium to the volatile tetrachloride which is condensed in a second vessel. The uranium can either be dissolved in nitric acid or converted to uranium hexafluoride by contacting with fluorine. In scouting corrosion tests in which 15 materials were exposed to hydrogen chloride and nitrogen-diluted carbon tetrachloride vapors, it was determined that the carbon tetrachloride part of the cycle was the most corrosive and that corrosion rates at 600°C were greater than 10 times the rate^{5, 58} at 400°C. Current results are shown in Table IV-12. Of the metals, it would appear that Nichrome-V holds the most promise.

Instrumentation and

Equipment Design

The effects of nuclear radiation upon several types of electrical components have been reported by Pfaff.⁶⁴ The performance of the components was measured both during their irradiation and after irradiation. All of the in-pile irradiations were performed in the CP-5 research reactor at ANL. The irradiation period varied between 7 and 10 days. Transformers, dynamotors, insulated wires, magnetic cores, and ferromagnetic materials were tested during this phase.

Transformers selected were hermetically sealed and encapsulated. Only the hermetically sealed units using wax and asphalt as potting

* The following definition of terms is used by the *Metals Handbook*: Impact extrusion = a cold forming process in which the metal is forced by impact to flow around the punch, forming a tube with a solid bottom. Ironing = thinning the walls of deep drawn articles by reducing the clearance between punch and die.

Table IV-12 CORROSION OF PROPOSED MATERIALS IN ZIRCEX PROCESS ENVIRONMENTS^{5,40} AT 600°C

Alloy	Observed corrosion, mils/month
<i>1-hr Exposure to CCl₄</i>	
Nichrome-V	5.5
Inconel	18
Chlorimet-2	32
Pyroceram 9608*	1.0
<i>13-hr Zircex Cycle†</i>	
S-816‡	29
Chlorimet-2	12
Hastelloy B	46
Stainless steel 316	20
Stainless steel 329	213

* A crystalline material made from glass described in Report PY-2, Corning Glass Works, Corning, N. Y.

† Zircex cycle: (1) HCl, 11 hr, 600°C; (2) CCl₄ vapor plus N₂, 1 hr, 600°C; (3) O₂, 5 min, 600°C; (4) N₂ plus CCl₄ vapor, 1 hr, 600°C.

‡ A cobalt alloy having the following composition (weight per cent): chromium, 20; nickel, 20; iron, 4; carbon, 0.38; manganese, 1.2; silicon, 0.4; molybdenum, 4; tungsten, 4; niobium + tantalum, 4; cobalt, 43 (by difference).

material ruptured. However, in all cases the electrical parameters remained unchanged.

Damages to hookup, aircraft, and magnet wires varied according to the insulation. Teflon-coated wire showed the greatest deterioration. Polyvinyl chloride and nylon insulations displayed fissures when subjected to flexibility tests. Magnet wire with Formvar and a combination of Formvar and nylon as insulation also showed damage. In some cases this type of insulation was unable to survive the specified dielectric breakdown voltages.

Dynamotors suffered primarily from lubricant deterioration, resulting in impairment of bearings.

Ferrites remained essentially unchanged during irradiation. Magnetic core material showed some decrease in flux density, and the coercive force usually increased.

Colvin⁶⁵ reported on the design of a colorimeter that measures the concentration of uranyl nitrate or plutonium nitrate in process streams in a field of high radiation. The instrument uses the dual-beam principle to compensate for darkening of optical components and for turbidity in the solution. A pulsating light source and a-c amplifiers are used in the measuring system to eliminate the drift that would result with a d-c system. A method of remote stand-

ardization is included in the instrument, which permits a periodic check and readjustment of the calibration.

The colorimeter was used to measure the concentration of either uranyl nitrate or plutonium nitrate in solution. The instrument was tested under plant conditions with calibrations in the range from 0.1 to 10 g of Pu(III) or Pu(IV) per liter and from 0.1 to 70 g of uranium per liter. The accuracy of the measurements was found to be limited by the effects of extraneous solution variables rather than instrument noise or drift. The combined noise and drift produced an error of about ± 1 per cent of the recorder span, whereas variations in temperature, turbidity, and nitric acid concentration in the solution can produce errors of 15 to 20 per cent of the span.

Remotely operated, semiautomatic machines, designed to effect the mechanical disassembly (i.e., decanning) of spent fuel elements from the EBR-II have been developed and are reported by Simon.⁶⁶ The machines described are laboratory models that have successfully decanned simulated fuel elements. They are electrically or pneumatically operated and are capable of decanning three fuel elements per minute without the routine use of manipulators. Each machine is made up of functional units which are sequentially placed to eliminate handling between steps of the decanning operation and which are easily removable for replacement or maintenance.

In the first of the two machines described, pneumatically operated devices prepare the fuel element for a rotary shearing operation which cuts the tubing jacket along a helical circumferential path as it is being removed. The alternate machine removes the jacket by means of a series of shearing rolls. Both machines are served by auxiliary mechanisms, such as inspection jigs, fuel and scrap choppers, and transfer magazines. Improved versions of these machines or machines employing alternate methods still under development are to be designed for installation in the fuel-cycle facility of the EBR-II plant.

Homogeneous Reactor

Fuel Processing

One of the potential advantages of the homogeneous reactor concept is the ability to with-

draw a side stream of fuel either continuously or on a batch basis for removal of fission-product poisons. The aqueous Homogeneous Reactor Test (HRT) at Oak Ridge is one such reactor, and a chemical processing plant has been installed in conjunction with it to exploit this advantage.

Insoluble fission and corrosion products are removed in this plant by a system of hydroclones. The original installation consisted of a single hydroclone, and operating experience indicated that it was not able to remove the solid constituents as rapidly as they accumulated. The system was modified by installing 12 hydroclones in parallel, the underflow of which fed the original single hydroclone. Solids concentrations in this unit were then dissolved in the normal manner. Operating experience with this system indicates further improvements are necessary. A revised multicclone assembly has been designed and is being fabricated for replacement during a shutdown period.⁶⁷ It is contemplated that efficiency for solids removal will be increased by several mechanisms. Reducing the size of the hydroclones from 0.6 to 0.4 in. will increase the removal efficiency for particles in the range of 0.5 to 1 μ by 50 to 100 per cent. To compensate for the reduced flow through each hydroclone, five additional hydroclones are being provided. A second method for increasing the efficiency is to increase the pressure drop across the multicclone from 48 to 94 ft of liquid head. The latter number represents the full head of the circulating pump. Collection efficiencies for 1- μ particles are expected to be increased from 30 to 50 per cent due to this factor alone. Further improvement is expected by returning the overflow from the collection hydroclone to the multicclone underflow receiver.⁵ In addition, a screen was placed in the feed line to remove particles larger than 0.030 in. in an effort to reduce the possibility of again plugging the feed ports.

Of considerable significance for the neutron economy of homogeneous reactors is the ability to control the Xe^{135} fission-product poison. Since each of the three major homogeneous reactor types (aqueous, molten salt, and liquid metal) has a potential for breeding new fuel, this becomes all the more important. Homogeneous reactors particularly lend themselves to continuous Xe^{135} removal, and it is not too difficult in each case to reduce the equilibrium

poison level* of Xe^{135} (5 per cent with no removal) by factors of 5 to 10. A discussion of the various methods of Xe^{135} control available for fluid-fueled reactors, together with the economic significance, is contained in a recent ORNL report.⁶⁸ The major conclusion of the report is that no significant differences in the minimum practical Xe^{135} poison level or the cost to achieve this level are evident for the various methods considered. All three systems have the capability of operating at Xe^{135} poison levels of less than 1 per cent, and the cost associated with accomplishing this is less than the value of the neutrons saved. From an economic viewpoint the power-cost value of the neutrons lost based on a U^{235} cost of \$17 per gram varies from 0.1 to 0.15 mill/kw-hr for thermal efficiencies of 40 per cent and about 25 per cent, respectively. In the case of the molten-salt and liquid-metal-fueled reactors, the Xe^{135} stripping system with appropriate gas-phase handling facilities is estimated to cost 0.05 to 0.08 mill/kw-hr. In the case of the aqueous homogeneous reactor, where at least a portion of the Xe^{135} would be removed in the form of the iodine precursor, similar costs would result. Should technological developments make possible the elimination of the gas-phase holdup and processing systems, a cost of 0.01 mill/kw-hr could be considered as being within reach. In all-out breeder systems where it would be desired to reduce the Xe^{135} poison level to less than 0.5 per cent, the diffusion of iodine into graphite may be limiting for the molten-salt and liquid-metal-fueled reactors.

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Section

V

WASTE DISPOSAL

Second AEC Meeting on Fixation of Radioactivity in Solid Media

An unclassified working meeting on radioactive waste management was held at the National Reactor Testing Station, Idaho Falls, Idaho, on September 27 through 29, 1960. The fixation or conversion-to-solid approach to the ultimate disposal of high-level waste was discussed. The objectives of this meeting were to summarize and assess the results of investigations since the first meeting held in 1957. The sessions were conducted on a panel basis and covered work on the following waste fixation subjects:

1. Conversion to solids and fixation methods:
(a) Calcination by fluidized bed, radiant-heat spray, pot, and rotary kiln and (b) ion exchange and sorption.
2. Off-gas cleaning.
3. Characteristics of solid and final disposal.
4. Construction materials.

The proceedings of this meeting are to be published and, when they become available, will constitute a valuable source of information on this subject.

Reduction to Solids

One of the most promising methods for treatment of high-level liquid radioactive wastes is conversion to solids by calcination. A number of calcination methods are under study, including the use of fluidized beds, heated pots, radiant-heated spray towers, and rotary kilns. Developments on these methods are reviewed below.

Work on the use of clays or minerals for the adsorption of activity is also discussed here.

The decontamination potential of several types of Italian bentonite clays¹ and the fixation capacity of acid montmorillonite clay in acid solutions of zirconium salts² have been reported in recent literature. The effects of some spray-column variables on radiant heat transfer in spray calcination were investigated for a thesis study,³ and a study of some of the fundamental kinetics of fluidized calcination of simulated aluminum type wastes has been reported in the literature.⁴ Solidification methods for Sulfex and Zirflex decladding wastes were also described.⁵

Adsorption on Natural Materials

Studies at Hanford of the use of the mineral clinoptilolite for decontamination of the condensate produced during self-evaporation of waste at the Purex waste tank farm were reported in a previous Review.⁶ Nonradioactive constituents and radionuclides in the condensate have been determined⁷ and are listed in Table V-1. A tap water feed containing stable cesium traced with Cs¹³⁷ was fed for a total of 50,000 column volumes to a 50-g bed of the mineral to determine its ultimate capacity for removing cesium. The decontamination factor was 6800 after passage of 9500 column volumes and 5100 after 13,600 column volumes to the end of the run. Plugging of the mineral bed with flakes of iron oxide from the water terminated the test. Experience indicates that plugging is more apt to limit the life of a mineral bed than is its adsorption capacity.

The use of chelating agents for suppressing ion interference in the processing of Purex type wastes on mineral clay columns for the removal of cesium and strontium has been investigated at Brookhaven National Laboratory (BNL).^{8,9} A synthetic waste solution containing iron, nickel,

Table V-1 RADIOACTIVE AND NONRADIOACTIVE CONSTITUENTS PRESENT IN CONDENSED VAPORS FROM PUREX BOILING HIGH-LEVEL WASTE TANKS⁷

Radioactive constituent	Concentration, $\mu\text{c/ml}$	Non-radioactive constituent	Concentration, mg/liter
Cs ¹³⁷	2.3×10^{-2}	TBP	30-190
Nb ⁹⁵	2.5×10^{-2}	Shell spray	<10
Zr ⁹⁵	1.2×10^{-2}	base	
Ru ¹⁰⁶	7.2×10^{-3}	Sodium	<1.5
Ru ¹⁰³	5.6×10^{-3}	Iron	0.1
Sr ⁹⁰	3.7×10^{-3}	Nickel	<0.01
Ce ¹⁴⁴	5×10^{-3}	Chromium	<0.01
Y ⁹¹	3×10^{-3}	Copper	<0.01
Gross β	9.1×10^{-2}	Zirconium	<0.01
Gross α	$<1.2 \times 10^{-6}$	Manganese	<0.01
		Cobalt	<0.01
		Calcium	<0.01
		Magnesium	<0.01

and chromium corrosion products with a slight excess of citric acid as the chelating agent and an Sr⁹⁰ concentration of 1.23×10^5 dis/(min)/(ml) was passed through six 4-ft-long by $\frac{5}{8}$ -in.-diameter columns of clinoptilolite in series. The temperature of the system was maintained between 40 and 50°C. The results indicated a slight chelation of the Sr⁹⁰, with the decontamination factors in the range of 1.25×10^5 . Greater decontamination factors, 3×10^5 , were obtained where the temperature was higher at the beginning and end of the run. Experiments were performed to determine the effect of concentration of chelating agents. The results and

Table V-2 EFFECT OF CITRATE CONCENTRATION ON Sr⁹⁰ DECONTAMINATION OF CITRIC-ACID-TREATED WASTE SOLUTION⁸

(Conditions: Feed Composition of 0.005M Fe, 0.0023M Sr with Added Sr⁹⁰ Tracer (3 to 5×10^5 dis/(min)(ml); Volume Passed; 3800 to 3900 ml; Separate Column 1 Ft Long Containing Clinoptilolite Exchanger; Temperature, Ambient)

Citrate concentration, M	Decontamination factor
0.0045	9×10^4
0.0050	8.2×10^4
0.0055	4.5×10^4

conditions are given in Table V-2. No explanation was offered for the relatively high (10^5 vs. 10^4) decontamination factor obtained when the

molarity of citrate equaled that of the added corrosion product.

BNL is also examining clinoptilolite for its suitability as an ion-exchange material for use at elevated temperatures and high pressures for the purification of the primary cooling water from pressurized-water-cooled reactors which operate with cooling water in the neighborhood of 335°C and 2000 psi.⁹

The use of calcined alumina and expanded vermiculite for the decontamination of low-level liquid wastes has been studied at ICPP.¹⁰ Distribution coefficients at pH 7.7 were determined for Sr⁹⁰, Cs¹³⁷, and Ce¹⁴⁴ with these two solid absorbents. For calcined alumina, the values for strontium, cerium, and cesium were 400, 1500, and 1, respectively; and, for expanded vermiculite, the values were 1500, 1000, and 1800, respectively.

Calcination

The Hanford fluid-bed calciner⁶ is being used to study particle growth while calcining wastes. The results of 18 runs (4 to 7 hr long) in the fluid-bed calciner (8-in.-square by 36-in.-high heating section), using a feed containing 2M aluminum nitrate, 1M nitric acid, and 0.15M sodium nitrate, and a feed rate of 10 to 18 liters/hr, have been reported.⁷ The bed temperature in all runs was 500°C. The superficial fluidizing-gas velocity was 0.4 to 0.7 ft/sec, and the atomizing air-to-feed volume ratios were 300 to 350. Average calcine particle size was varied from undesirably large to undesirably small by varying the atomizing air-to-feed ratios and fluidizing-gas impingement velocities. Excessive attrition rates were obtained at atomizing air-to-feed volume ratios of 350 and fluidizing-air impingement velocities of about 500 ft/sec. In contrast, with all other conditions equal, excessive particle growth occurred with atomizing air-to-feed ratios of 640 and fluidizing-air impingement velocities of about 90 ft/sec. The fine particles removed from the calciner off-gas stream by the "scalping" cyclone represent 3 to 20 wt.% of the solids in the calcined product and have an untapped bulk density of 0.1 to 0.3 g/cm³. Two runs, using superheated steam as the fluidizing gas, were successful. The use of steam as fluidizing gas would decrease considerably the amount of noncondensables in a calciner off-gas system.

The behavior of cesium and ruthenium was determined⁷ in one run of the Hanford radiant-heat spray calcination unit.⁶ Nonradioactive ruthenium and cesium were added to a feed simulating Purex 1WW (first-cycle waste) which has been "acid-killed" with formaldehyde, concentrated by a factor of 2, and neutralized. Only 1.6 per cent of the ruthenium and less than 2.1 per cent of the cesium was detected beyond the off-gas filter.

Laboratory-scale batch calcination studies of simulated Purex type wastes were also made at Hanford.⁷ The relative concentrations of the major constituents (sodium, iron, aluminum, sulfate, and nitrate) were varied from run to run to determine the effect on operation of the heated 3-in.-diameter by 7-in.-high stainless-steel pot and to determine the effect on the product properties. The unagitated pot was fired to a terminal internal temperature of 800 to 900°C. At sulfate to salt nitrate mole ratios greater than 1, a melt formed at temperatures of 750 to 850°C. As the ratio increased, the viscosity of the melt decreased. The specific gravity of the solidified melts was 2 to 2.6. With the sulfate to salt nitrate ratio less than 1, the solids did not melt at temperatures less than 900°C, and the fired solids were porous with densities of 1.1 to 1.9 g/cm³. With sulfate to salt nitrate ratios of 0.5 and higher, solids coated the pot wall during feed addition, promoting foaming and bumping because of the reduced effective pot diameter. No noticeable pot corrosion was observed during the runs reported.

At ORNL a process for converting wastes to solids by pot calcination is being investigated.¹¹ In the current work at ORNL on this process (Fig. 10), waste that has been stored three or more years for decay of short- and intermediate-lived fission products is fed to an evaporator where the volume is decreased by factors of 2 to 4. The overheads from the evaporator go to an acid fractionation column that produces concentrated acid for recycle to the chemical plant and a very dilute low-radioactivity-level waste that can be further decontaminated before disposal. The evaporator bottoms, in the form of a very concentrated solution or slurry, go to an electrically heated cylindrical pot for evaporation to dryness and calcination at temperatures of 700 to 900°C. The calciner off-gases are first passed through a downdraft condenser where 85 to 95 per cent of the nitrogen

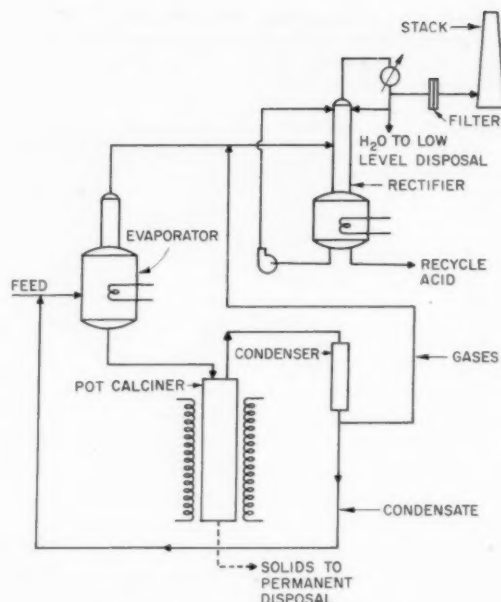


Figure 10—Flow sheet for converting high-level wastes to solids by pot calcination.⁵

oxides are absorbed in the condensing water and then to the acid still for recovery of the remainder. The condensate is recycled to the evaporator, and the gaseous inerts in the system are removed in the reflux condenser of the acid rectifier, filtered, and then released through a stack. When the pot is filled with calcined solids, connecting process lines will be broken, and the pot will be sealed, removed from the furnace, and shipped to a permanent storage site.

The feasibility of pot calcination in terms of the rate of calcination and rate of heat dissipation during storage has been established. Tests with Purex waste indicated that the effluent from the processing of 6 tons of uranium could be calcined and contained in one pot, 10 in. in diameter by 6 ft long.⁵ The problems of heat dissipation during permanent storage in various natural environments have been reported.¹² The diameters of the calciner pots are to be limited to 15 in. to permit heat dissipation by natural convection rather than by forced cooling.

Evaporation and calcination to 900°C of synthetic high-level wastes were studied in pots of two sizes. In the smaller equipment (4 in. in diameter, 18 in. long), a volume-reduction factor (volume of feed per bulk volume of solid

residue) of 8.4 was obtained with a synthetic Purex 1WW concentrated feed with sodium hydroxide and calcium hydroxide added to the waste to reduce sulfate volatility. The solid residue had an apparent density of 1.56 g/ml, equivalent to a porosity of about 48 per cent. The condensate and off-gas contained 98 and 2 per cent, respectively, of the nitrate, and 0.7 and 0.02 per cent, respectively, of the sulfate originally present in the waste. Approximately 5 liters of noncondensable off-gas, principally oxygen, was collected per liter of waste. In similar experiments with nitric oxide (NO) admitted during the run, added with the intent of decreasing ruthenium volatility, the production of noncondensable off-gas was decreased to almost zero. In the larger equipment (6 and 8 in. in diameter, 78 in. long), experiments were conducted with synthetic Purex 1WW waste and concentrated Darex waste. With the Darex waste, the density of the calcined solids was 0.8 g/cm³, compared with 1.5 g/cm³ for the calcined Purex waste.

In investigations of waste calcination at ORNL, no exothermic and/or violent reaction was observed in batch evaporations and calcinations to 400°C of simulated Purex 1WW containing 3 to 300 ml of TBP per liter of waste. Measured thermal conductivities of calcined wastes varied almost linearly with temperature from 0.210 Btu/(hr)(ft)(°F) at 90°F to 0.311 Btu/(hr)(ft)(°F) at 1329°F for calcined Purex waste and from 0.140 Btu/(hr)(ft)(°F) at 92°F to 1.52 Btu/(hr)(ft)(°F) at 1600°F for a calcined Darex waste. Evaporation and calcination of Purex 1WW in a nitric oxide atmosphere decreased the ruthenium in the condensate from about 70 to between 0.9 and 1.5 per cent without additives and to 1.9 to 32 per cent with additives. The presence of about 2 ml of TBP per liter of waste decreased the amount of ruthenium in the condensate, in an air atmosphere, from about 70 to between 4 and 15 per cent, depending on additives; and decontamination of an air stream bearing a soluble aerosol by a packed scrubber was as much as 1000 times more effective when steam was present in the vapor phase.

ICPP laboratory test data indicate that the useful life of a silica-gel bed for the adsorption of volatile ruthenium from the calcination of acidic aluminum nitrate wastes may amount to many adsorption-desorption cycles.¹³ At least 40 to 50 days of operation on one column of silica gel in the ICPP demonstration calciner

appears feasible. The removal efficiency of silica gel was also shown to decrease with successive wetting and drying cycles.¹⁴ This is not expected to have a significant effect on the operation of the demonstrational unit. Electrostatic precipitators were found to have a higher removal efficiency for solid particles (alumina) when a wetted wall rather than a dry wall type was used.¹⁴ For the wetted-wall type precipitators operating at a potential of about 20 kv, the removal efficiencies were over 99 per cent for particles larger than 0.3 μ and 93.8 per cent for particles smaller than 0.3 μ . For the dry-wall type operating at a potential of 24 kv, the efficiencies were over 97 and 86.8 per cent, respectively. Qualitative tests have indicated that, if NaK should leak into either the pilot plant or demonstrational calciner, the reaction between NaK and oxygen from the air would predominate and is unlikely to be of an explosive nature.

Studies are under way at the ICPP to find methods for treating the zirconium wastes from the currently used hydrofluoric acid dissolution-solvent extraction process for zirconium fuels in order to reduce the aqueous storage volume. Head-end treatment or conversion of the waste to a solid is being examined.^{10,14,15}

The removal of cesium and other long-lived radioisotopes from process waste solutions prior to calcination would simplify the requirements for storage of the calcined product.¹⁵ Ammonium phosphomolybdate, used as an inorganic ion-exchange material, was shown to have high affinity for cesium in acid solutions and in the presence of aluminum nitrate and to have reasonable stability in mineral acids, other than hydrofluoric acid, up to 1.0 N acid.

To reduce the leachability of soluble fission products from calcined aluminum oxide wastes, a method under consideration at ICPP is to produce an impervious coating on aluminum oxide by the application of metal or ceramic coatings from a powder-metallizing gun in a fluidized bed followed by a heat-treatment of the particles.¹⁴ Also of interest is a ceramic-coating technique for radioisotopes in tiny spherical form developed by Minnesota Mining & Manufacturing Company.¹⁶ The technique chemically seals the isotope in ceramic spheres of 10 to 100 μ .

Ultrasonic leaching experiments of simulated calcined wastes have demonstrated that approximately 95 to 100 per cent removal of the

radioactivity can be achieved in 24 to 30 hr with continuous ultrasonic treatment compared with 10 to 14 days to remove 90 per cent by non-ultrasonic methods.¹⁷

Experimental measurements of the heat-generation rate in a second ICPP 300,000-gal high-activity-waste storage tank were attempted.¹⁰ A heat-generation rate of about 2.5 Btu/(hr)(lb alumina) was determined for this tank, which contained high-activity aluminum process waste less than six months old.

Separation of Specific Isotopes

The AEC issued a short report in which the current status of possible large-scale uses of separated fission products was reviewed.¹⁸

ORNL has proposed a solvent-extraction process and ion-exchange scheme for the recovery of Sr⁹⁰ and rare earths from Purex wastes.⁵ In the solvent-extraction process, the iron in the waste is first complexed with tartrate, and the pH is adjusted with caustic. Strontium and rare earths are extracted by a solvent comprised of di-2-ethylhexyl phosphoric acid-tributyl phosphate-Amsco 125-82 and are stripped with nitric acid. Processing and strip product through additional solvent-extraction cycles yields separate concentrated strontium and rare-earth fractions. For separating the strontium and rare-earth products by ion exchange, the hydrogen form of Dowex 50W X-8 (20 to 50 mesh) is used. The Purex waste solution is diluted by a factor of 10, and oxalic acid is added prior to pumping it through a column of the resin. Strontium is separated from rare earths by eluting with 1M nitric acid and passing this product stream through a second resin column. The rare earths are recovered by eluting with 0.5M monosodium citrate (pH 3.5). Strontium is recovered by eluting with 1M NaCl and 0.07M sodium versenate at pH 6.1.

A comprehensive report has been issued by Radiation Applications Incorporated on foam separation (described in a previous Review)¹⁹ as applied to the removal of strontium and cesium from Purex type waste streams.²⁰ Detailed data are given showing the effects of chemical and operating variables on enrichment values. A tabulation of the various complexing and foaming agents is given. Work has been done on the development of continuous foam

separation, as well as on single-column and multiple-column separation.

Additional literature on the separation and purification of several isotopes (Cs¹³⁷, Tc⁹⁹, and Pm¹⁴⁷) by precipitation, solvent-extraction, and ion-exchange methods (see page 23) are available for the interested reader.²¹⁻²⁴

Final Disposal Methods

Soil chemistry studies²⁵ are being carried on at Hanford^{26,27} in support of the disposal of low- and intermediate-level liquid wastes to the ground. Information on the nature of liquid flows through various types of soil has been obtained, and an equation has been developed for the flow of fluids through unsaturated soil.²⁸

In soil column studies with radiostrontium, the effects of temperature (18 to 83°C), of species of accompanying ion, and of soil column length and diameter were studied. It was learned that temperature can have a significant effect on the soil sorption of radionuclides. Species of accompanying ion determines the direction and amount of the effect. If the ion accompanying strontium is sodium, increased temperature improves strontium sorption; whereas, if the accompanying ion is magnesium or aluminum, the opposite is true. Where calcium is the accompanying ion, no measurable effect is seen. Where cesium is the trace ion, elevated temperatures would always decrease soil sorption. At equal temperatures, calcium and aluminum are strong competitors for exchange sites, and sodium is a weak competitor. Therefore about 20 times the crib capacity could be expected for waste neutralized with caustic rather than with limestone. The soil column diameter was found to have no effect on the shape of strontium breakthrough curves. Soil column length, on the other hand, had a pronounced effect on the shape of the breakthrough curves.

The storing of liquid radioactive waste products from nuclear reactor fuel-processing plants in salt mines and shallow sedimentary formations has been proposed as a method of ultimate storage.²⁵ The chemical reaction between nitric acid and sodium chloride has been investigated to determine what could be expected when an acid waste solution is stored in salt mines.²⁹

A University of Texas study³⁰⁻³² indicated that it is feasible to store reactor fuel wastes

in washed-out cavities of salt domes to a depth (less than 3000 ft) where the differential in pressure between the soil overburden pressure and pressure of the fluid inside the cavity does not exceed 3000 psi and the temperature is less than 400°F. The testing of actual cavities under the earth's overburden pressure and the earth's normal temperature show that no permeability of salt exists in place. The cost of completing underground storage cavities in salt masses is expected to be approximately \$1.05 per barrel of storage space. The principles for designing salt cavities for storage of radioactive wastes are detailed.

In its investigation, the Bureau of Mines³³ concludes that the use of shallow sedimentary formations, including partly depleted oil-productive sands, in some areas where geology permits, is feasible and that, to demonstrate that feasibility, field pilot plants can be constructed using available information.

Disposal of radioactive wastes into the sea was discussed in an earlier Review.⁶ AEC standards for sea disposal are based on the fact that the ocean water will safely dilute and disperse the low-level wastes that are permitted to be disposed of at sea. The Commission, as a conservative approach, requires disposal at not less than 1000 fathoms; and, in a recent decision in a waste-disposal case,⁶ the AEC stressed confining the wastes until the containers reach this required disposal depth. A procedure has been developed for the sea disposal, by fixation in concrete with Portland cement, of ion-exchange resins containing sorbed fission products and filtered corrosion products formed in the operation of nuclear merchant ships of the N.S. *Savannah* type.^{5,34} In a leaching test with simulated sea water, only 0.44 per cent of the gross gamma activity was leached out after a contact time of 2540-hr duration. The data indicate that little or no further leaching will occur.

Other Literature

The radioactive waste-disposal system planned for the Pathfinder Atomic Power Plant has been reported.³⁵ Details have been reported on the development of prototype equipment and processing systems to prevent atmospheric contamination from organic vapors or radioactivity present in the waste gases produced

during all phases of the operation of the Piqua organic-moderated reactor.^{36,37} For the CNA (Centrale Nucléaire des Ardennes) organic-moderated reactor, the normal radioactivity and associated radiation levels in the primary coolant and in the waste-disposal system have been calculated.³⁸ Information has been made available on an axial-flow magnetite bed filter that can effectively remove radioactivity and insoluble corrosion products from a pressurized-water reactor coolant.³⁹ In actual practice, conventional water- and sewage-treatment processes have demonstrated their effectiveness for the removal of radionuclides present in a municipal water supply and in sewage.⁴⁰

An incinerator has been placed in operation by the General Electric Company at its San Jose, Calif., fuel-fabricating center.⁴¹ The incinerator features (1) a high-temperature furnace box that completely burns all combustible material, (2) spray-cooling equipment, and (3) a high-efficiency filter system for cleanup of the radioactive particles in the exhaust gases. It is expected to reduce the cost of disposing of contaminated wastes by 75 per cent. Design and operational details of the filter media used for nuclear energy air-cleaning applications in the United Kingdom are reviewed in two British journals.^{42,43}

The Vitro Corporation of America is to undertake for the AEC an operation research study to define the optimum system for disposal and treatment of radioactive wastes.⁴⁴ Two bibliographies of references to reports and published literature have been compiled by the AEC to serve as guides in the fields of fission-product fixation⁴⁵ and radioactive waste processing and disposal.⁴⁶

A study of the economics of permanent tank storage of power-reactor fuel-processing wastes indicated⁵ that storage costs should average 0.05 to 0.23 mill/kw(e)-hr (see Table V-3).

Savings have been made in the construction costs of Savannah River Plant tanks for the storage of low-level radioactive waste solutions.⁴⁷ While still conforming to the principle of total confinement, this saving was brought about by the elimination of a number of features found in the tanks designed for storing high-level radioactive wastes, e.g., cooling coils, and the annular space and secondary saucer container. The low-level activity tanks have a nominal capacity of 1,300,000 gal each.

Table V-3 SUMMARY OF WASTE-STORAGE COSTS FROM FUEL PROCESSING FOR VARIOUS REACTOR TYPES⁵

Type of waste	Volume stored, gal/metric ton of U or Th	Storage cost for Case 1 (35% return on investment)*		Storage cost for Case 2 (10% return on investment)†	
		Dollars per gallon	Mills/kw(e)-hr	Dollars per gallon	Mills/kw(e)-hr
Uranium Converters					
Zr-clad UO ₂					
Zirflex decladding waste	2120	3.14	0.1109	2.03	0.0717
Purex solvent-extraction raffinate	60	22.37	0.0224	12.21	0.0122
		25.51	0.1333	14.24	0.0839
Stainless-steel-clad UO ₂					
Sulfex decladding waste	1100	3.84	0.0704	2.47	0.0453
Purex solvent-extraction raffinate	60	22.37	0.0224	12.21	0.0122
		26.21	0.0928	14.68	0.0575
Thorium Converters					
Zr-clad ThO ₂ -UO ₂					
Zirflex decladding waste	2120	3.14	0.0555	2.03	0.0358
Thorex solvent-extraction raffinate	640	15.60	0.0833	8.69	0.0464
		18.74	0.1388	10.72	0.0822
Fast Breeders					
Stainless-steel-clad UO ₂ -PuO ₂					
Sulfex decladding waste	1100	3.84	0.0857	2.47	0.0552
Purex solvent-extraction raffinate	60	22.37	0.0270	12.21	0.0148
		26.21	0.1127	14.68	0.0700
Thermal Breeders					
Aqueous UO ₂ SO ₄ solution					
Thorex solvent-extraction raffinate	640	15.60	0.2288	8.69	0.1275

* Assumes that the waste-storage system was owned and operated by a chemical company without government guarantees or subsidization.

† Assumes government type financing. In this case, a 10 per cent return on the investment resulted in about a 3.6 per cent return after taxes and expenses.

One study has concluded that it is not feasible to reduce the cost of waste disposal by utilizing the energy of the decaying fission products for the production of useful heat.⁴⁸

The AEC announced that arrangements have been made for public reporting, on a regular basis, of radioactivity data collected in the vicinity of major AEC installations.⁴⁹ The data are produced from routine monitoring programs at Commission-owned plants and laboratories where operations are of such nature that plant-perimeter radioactivity monitoring surveys are required. Environmental radioactivity data for the Hanford and Savannah River Plant areas and the levels of Sr^{90} activity, which were determined for the major surface waters of the United States, have been reported.⁵⁰⁻⁵² The

procedures used by Atomics International for analyzing surface-water samples taken before and after sea disposal of their radioactive wastes are described in a recent report.⁵³

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Section VI

PRODUCTION OF URANIUM, THORIUM, PLUTONIUM, AND THEIR COMPOUNDS

Uranium

Production Facilities at Springfield

(Great Britain)

A major expansion of capacity, authorized in 1955, for producing uranium fuel elements at Springfield has resulted in the construction of a new uranium plant. A series of three recently published¹⁻³ articles presents some details of the plant design and the various processing steps. Where feasible, continuous operation has replaced batchwise processing previously used. Large, continuous box extractors are used in purifying uranyl nitrate solutions with tributyl phosphate. To avoid accumulation of uranium-bearing solid residues from the processing of uranium ore concentrates, an integrated process has been set up to recycle streams of solid residues.² For the reduction to metal, calcium has been replaced by the cheaper reductant magnesium.¹ Fluidization techniques have been employed in the production of uranium trioxide, reduction to uranium dioxide, and hydrofluorination to uranium tetrafluoride.³ Although these fluid-bed operations are now conducted as batch operations, continuous operation is contemplated in the immediate future. A brief description of the Springfield fluid-bed processes appeared in a previous Review.⁴

Uranium Dioxide Production

Flame Denitration of Uranyl Nitrate Liquors. Pilot-plant facilities have been installed at the Mallinckrodt Chemical Works to study the one-step conversion of uranyl nitrate liquors to uranium dioxide.⁵ Estimates made on this process indicate that uranium dioxide produced by flame denitration would incur lower operating costs than the combined costs for the present

batch denitration and fluid-bed reduction processes. The concept involves atomizing aqueous uranyl nitrate directly into a reducing flame of gaseous fuel. Since the residence time of the liquid in the high-temperature zone is very short, good atomization of the liquid is necessary to provide a large surface area for heat transfer. Several nozzle and burner configurations were investigated;⁶ and, in the final design, the burner surrounded the nozzle and the liquid feed was introduced along the burner axis. Droplet size of about 40 μ or less was required.

Both concentrated and dilute (65 wt.%) uranyl nitrate solutions have been successfully reduced to a uranium dioxide powder in the flame reactor.⁶ Successful operation required a 20 per cent excess of propane, a 980°C exit-gas temperature, and a residence time for both gases and solids in the reactor of $\frac{1}{4}$ sec. The uranium dioxide product was in the form of a fine powder with a particle size identical to micronized uranium dioxide now being produced at Mallinckrodt. Sintered pellets of 96 per cent of the theoretical density have been prepared from flame-reduced uranium dioxide. X-ray analyses indicated that the composition of the uranium dioxide lies between $\text{UO}_{2.00}$ and $\text{UO}_{2.01}$. The product was more reactive to hydrogen fluoride than oxides produced by other processes. Flame-produced oxide should be readily hydrofluorinated in the cascade screw reactors now employed in the production of uranium tetrafluoride.

Reduction of a Molten Uranyl Chloride Salt Solution. A dense, crystalline precipitate of pure uranium dioxide can be prepared by the reduction of uranyl chloride contained in a molten-salt solution.⁷ The uranyl chloride solution was prepared by adding uranium trioxide

to a eutectic of potassium chloride and sodium chloride and chlorinating with chlorine gas at 800°C for 2 to 3 hr. Other uranium oxides, uranium dioxide or uranous oxide (U_3O_8), can also be chlorinated in molten halide salts to produce uranyl chloride. The reduction of uranyl chloride in the melt was accomplished (1) by contacting the solution with any of several metals, (2) by reaction with hydrogen or dry ammonia, or (3) by electrolysis. Among the metals found effective in precipitating uranium dioxide were bismuth, lead, tin, cadmium, zinc, and magnesium. The uranyl chloride reduction procedure was previously described in greater detail in Sec. IV, page 33.

Electrolytic reduction of uranyl chloride was found to be the most successful method for preparing crystalline uranium dioxide. The electrolysis was carried out between graphite electrodes at a potential of 2 to 3 volts and a cell temperature of 725°C. Uranyl ions are discharged at the cathode, and chlorine is liberated at the anode. Crystalline deposits of uranium dioxide are formed on the cathode surface. An equimolar solution of sodium chloride-potassium chloride containing 10 per cent uranyl chloride was used as the electrolyte. Formation of uranium tetrachloride near the end of the reduction limited to 90 per cent the conversion of uranyl chloride to uranium dioxide.

The electrolytic uranium dioxide was a coarsely crystalline material of density 10.7 to 10.9. Most of the crystals were larger than 150 mesh. Microscopic examination showed that the product consisted of small clusters of relatively large single crystals. Although this method was developed to recover pure uranium dioxide from spent oxide fuel elements, the technique might be applied to preparation of ceramic fuels.

Preparation of Spheroidal Oxide. Uranium dioxide used in dispersion type fuel must be strong, free flowing, and possess a high density. Ideally, the oxide should be in the form of uniform spheres. Exploratory work was performed to produce uranium dioxide particles by precipitation methods.⁸ Uranate type precipitations were employed, since these consistently produced higher density uranium dioxide than other source materials. Spheroidal uranium dioxide particles of greater than 98 per cent of the theoretical density have been produced by precipitating ammonium polyuranates from uranyl

nitrate solutions. The final particle size and shape are governed by the size and shape of the agglomerates formed during precipitation.

Precipitation was accomplished by adding 14M ammonium hydroxide to uranyl nitrate solutions containing up to 0.5M uranium at 70°C. The addition of small quantities of acetone or sulfuric acid to the uranyl nitrate solution tended to produce larger agglomerates during precipitation. Uranium dioxide spheres were prepared by drying the precipitate, followed by pyrolysis, and then firing in a reducing atmosphere. The average size of the agglomerates produced was approximately 60 μ , with a possible range of from 10 to 840 μ .

Fluidized-Bed Coating of Uranium Dioxide. Encapsulation of nuclear fuel elements has become the established method of maintaining mechanical integrity and assuring fission-product retention. Attention has been directed toward developing methods for coating individual particles of ceramic fuels such as uranium dioxide. Workers at Battelle Memorial Institute⁹ have demonstrated that a nonporous coating of metal can be applied chemically to individual particles of uranium dioxide in a fluidized bed. The work was performed in quartz or Vycor reactors 1 in. in diameter with uranium dioxide particles ranging from 88 to 177 μ .

Niobium metal was successfully deposited on uranium dioxide by reacting a mixture of hydrogen and niobium pentachloride at a bed temperature of 850°C. The rate of niobium deposition on a 100-g bed of uranium dioxide in the 1-in. column was limited to about 5 g/hr; higher rates often produced porous coatings. Leaching tests performed on coated oxide with 50 per cent nitric acid solution showed that coatings of less than 8 μ in thickness tend to be porous. Consistently good product was obtained with coatings 8 to 24 μ in thickness. Successive coatings can be applied to particles, but a void structure was frequently observed between the coating layers. Photomicrographs of coated particles showed the deposits to be very uniform, dense, and impervious.

Similar results were obtained in depositing molybdenum and tungsten on uranium dioxide. Molybdenum pentachloride and tungsten hexachloride were used as feed materials. No difficulty was encountered in either preparing a pure metal coating or overcoating a niobium-coated uranium dioxide powder with a 1- μ -thick layer of metal.

Several methods of coating uranium dioxide with chromium metal were given cursory investigation.⁹ Of the methods tried, only hydrogen reduction of chromous iodide was successful. Since chromium coatings that were applied to uranium dioxide surfaces were spotty and discontinuous, indicating poor nucleation characteristics of uranium dioxide for chromium, it was necessary to apply the metal to a substrate of niobium. Continuous chromium layers were obtained on niobium underlays by reducing chromous iodide in a fluidized bed at 850°C.

Carbon coatings have been applied to uranium dioxide particles by the pyrolysis of hydrocarbons in a fluidized bed. At temperatures in the range of 1000 to 1200°C, acetylene is superior to methane, benzene, or propane in terms of coating rate and freedom from soot. Uniform coatings were obtained in preliminary runs; and, as in the case of niobium, coatings less than 8 μ in thickness were found to be porous.

Physical Properties. A compendium on the physical properties of uranium dioxide has been published recently.¹⁰ Since the behavior and many of the characteristics of uranium dioxide depend upon variables inherent in the raw material, processing, powder preparation, and sintering treatment, it is often not easy to compare experimental data obtained by various investigators. Therefore the data presented in this book¹⁰ are also accompanied by a complete history of the material. The subjects discussed include preparation of uranium dioxide, physical properties, effects of particle characteristics, and binary-phase diagrams.

Uranium Tetrafluoride Production

Utilization of the Hydrogen Fluoride-Water Azeotrope. Large-scale uranium tetrafluoride production from uranium dioxide involves the consumption of a considerable quantity of anhydrous hydrogen fluoride. Since an excess of hydrogen fluoride is required in the process, economics dictate that by-product hydrogen fluoride be recycled instead of being discarded or sold. In order to minimize reagent excess, the concept of recovering and recycling hydrogen fluoride as a 38 per cent hydrogen fluoride-water azeotrope has been investigated.¹¹ A description of preliminary work appeared in a previous Review.¹²

The conversion of uranium dioxide to uranium tetrafluoride takes place in three screw reac-

tors operated in a cascade arrangement with uranium dioxide fed to the drive end of the first reactor and anhydrous hydrogen fluoride fed to the discharge end of the third reactor. Recycled azeotropic acid is introduced into the dilute acid section of the system at the powder-discharge end of the first reactor. The off-gas from the screw reactors is filtered, condensed, and reconcentrated to 38 per cent hydrogen fluoride in a Karbate distillation column.

The distillation column is a bubble-cap tower, 32 in. in internal diameter, with 14 plates on an 18-in. spacing. The 38 per cent azeotrope is drained from the stillpot to rubber-lined storage tanks. Overheads, which contain a trace of hydrogen fluoride, are condensed and either discarded or refluxed to the top plate. Depending on the acid content of the off-gas, the feed stream may be fed to any one of four plates in the column.

Operation of the screw reactors using this recycle technique has been successful at a production rate of 850 lb of uranium tetrafluoride per hour. Conversion levels of 97 to 98 per cent are routinely maintained. By incorporating the azeotrope recycle, the excess of hydrogen fluoride has been reduced to 10 per cent, and further reductions are expected. The rate of azeotrope recycle was 13.5 lb of 38 per cent hydrogen fluoride per 100 lb of uranium tetrafluoride. The rate of recycle of recovered acid is somewhat limited by reactor inlet pressure. By redesigning the present units to provide lower reactor backpressure, it is expected that an azeotrope recycle rate can be accommodated such that the over-all hydrogen fluoride consumption will drop to the stoichiometric requirement.

The savings realized by employing the azeotrope recycle flow sheet have been estimated to be approximately \$110,000 per year over the use of the next most economical flow sheet, based on a yearly production rate of 5000 tons of uranium.

Uranium Hexafluoride Production

Recovery of Uranium Hexafluoride and Fluorine in a Fluidized Bed. In the manufacture of uranium hexafluoride at the Portsmouth Feed Manufacturing Plant, uranium tetrafluoride powder is contacted with elemental fluorine in a flame reactor.¹³ The product gas is passed through cold traps to remove uranium hexa-

fluoride and then through a reactor where the gas is contacted with uranium tetrafluoride to remove fluorine. After passing through a second cold trap, the gas is vented to the atmosphere. For reasons of health and economy, it is desirable to minimize the amounts of reactive gases in the exhaust gas. An earlier Review¹⁴ discussed the successful removal of uranium hexafluoride and fluorine from vent gases by the use of a fluidized bed of uranium tetrafluoride. A similar process was recently studied at the Portsmouth plant.¹³ A 4-in.-diameter fluidized bed of uranium tetrafluoride with a bed depth of 7 in. was found effective in removing both uranium hexafluoride and fluorine from gases containing approximately 5 per cent fluorine and 0.5 per cent uranium hexafluoride. Uranium tetrafluoride was continuously fed to the fluidized-bed reactor at rates varying from 7 to 180 g/min. At bed temperatures above 350°C, the outlet fluorine concentration decreased sharply. Removal of uranium hexafluoride was most effective at temperatures below 300°C. Neither the uranium tetrafluoride feed rate nor the inlet gas flow rate seemed to affect the removal of uranium hexafluoride or fluorine from the gas stream.

Preparation of Uranium Carbide

At the present time the Reactor Development Division of the U. S. Atomic Energy Commission is supporting several programs intended to develop and evaluate bulk uranium carbide as fuels. Although some research has been conducted on various methods for preparing uranium carbide, methods for commercial preparation of uranium carbide powder are lacking. The preparation methods now being studied include the reaction of uranium metal with hydrocarbons and the reaction of uranium metal and uranium oxides with carbon.¹⁵ The reactions of uranium metal powder with methane or propane have been successful in preparing rather pure uranium carbide, with the only impurity being free carbon.¹⁵ In order to achieve greater reactivity of the uranium metal, it has been found necessary to convert the metal to powder by hydriding at 200 to 250°C. The reaction with methane is carried out at 650 to 700°C. It may be necessary to hydride unreacted metal after the reaction is partially completed to maintain a loose product and ensure complete reaction.

Propane and butane have been found to show greater reactivity than methane in the prepara-

tion of uranium carbide.¹⁶ The proposed mechanism of the reaction is the production of free radicals by the decomposition of the hydrocarbons. Since free radicals are very reactive, the formation of uranium carbide can occur at much lower temperatures as compared with the reactions involving carbon and uranium metal or carbon and uranium oxides. Uranium carbide was formed at 10°C by the reaction of uranium powder with free radicals produced in an atmosphere of propane by gamma radiation from Co⁶⁰.

Above 900°C the reaction of uranium metal with methane or propane leads to the formation of uranium dicarbide.^{16,17} The dicarbide species will react with uranium metal to form uranium carbide. This reaction may be employed to prepare pure uranium carbide from reaction products which contain a substantial amount of the dicarbide.¹⁷

The reaction between uranium dioxide and carbon at high temperatures (>1700°C) has been studied, but the product is a clinker of low density and is often not pure.^{15,18}

Several other processes are being considered to prepare uranium carbide. A reaction which appears favorable thermodynamically, and which may also be more economical, is the reduction of uranium hexafluoride with calcium and calcium carbide. A possible disadvantage to this process would be the difficulty of separation of uranium carbide from the other reaction products.¹⁵

Uranium Metal Production

A volume on the technology of uranium production, part of the National Nuclear Energy Series, has been declassified recently.¹⁹ Although it is somewhat dated, the book presents an accurate account of the research and development on uranium processing from ore to metal prior to 1951.

Coreduction of Uranium Alloys. Various alloys of uranium have been produced at the Paducah Metals Plant of the Union Carbide Nuclear Company by the coreduction techniques.²⁰ Especially in the case of zirconium, this method obviates the safety hazards associated with the preparation of alloys by remelting of sponge metals.

Four different alloys of uranium and molybdenum (3, 6, 10, and 14 per cent molybdenum) were prepared by coreduction with magnesium in a

steel bomb. The process conditions were established in batch operations producing 320 lb derbies. By varying the blends of molybdenum metal and molybdenum trioxide with uranium tetrafluoride in the bomb charge, all the alloys were successfully produced. The weight ratio of molybdenum to molybdenum trioxide employed increased from approximately 0.8 for a 2 per cent alloy to 4.7 for the 14 per cent composition. The quantities of the different blends used in the various alloy compositions tend to balance the heat evolved during the reduction. The furnace temperature for all runs was 670°C. Approximately 3 per cent excess magnesium was employed, and metal yields averaged over 95 per cent.

A 2 per cent zirconium-uranium alloy was produced by reducing a mixture of uranium tetrafluoride and zirconium tetrafluoride with 3 per cent excess magnesium. Both visual and chemical analyses indicated that zirconium segregated at the top of the derby. The remelted and cast ingot showed uniform zirconium composition.

Plutonium

Plutonium Metal and Alloys

Electrorefining of Plutonium Metal. Plutonium metal of excellent purity can be produced from bomb reduction metal by an electrorefining procedure.²¹ The electrolyte was a molten salt containing 10 wt.% Pu(III) chloride, 50.4 wt.% potassium chloride, and 39.6 wt.% sodium chloride. A massive cylinder of plutonium metal or alloy served as the anode, and a tungsten tube immersed in the electrolyte was the cathode. The electrorefining cell was mounted in a tube furnace. During operation, plutonium was oxidized at the anode, entered the molten-salt electrolyte, and was reduced back to metal at the cathode surface. Because the cell was operated at 700°C, above the melting point of plutonium, the dense cathode deposit drained continuously down into an annular space around the anode compartment. In the cell designed for continuous refining, an overflow weir was constructed beneath the anode to allow continuous withdrawal of purified metal.

The results from several preliminary runs indicated that plutonium metal of greater than 99.98 per cent purity could be consistently prepared by electrorefining on a 100-g scale. The

only detectable impurities were calcium, aluminum, tungsten, carbon, and oxygen. The quantity of aluminum present could probably be reduced by coating with calcia the alumina crucibles used as the cell containers. A single run was made with a plutonium-iron alloy anode containing 2.54 per cent iron. The iron content of the purified product was reduced to 0.018 wt.%. Therefore, plutonium-rich iron alloy scrap can probably be recovered directly by electrorefining.

Preparation of Plutonium Alloys. Binary plutonium alloys of several metals may be prepared by reducing plutonium fluorides or oxide with an excess of the alloying metal. The reaction of aluminum with plutonium trifluoride and plutonium dioxide has been studied in detail.²² The aluminum reduction of plutonium trifluoride was dependent upon the removal of gaseous aluminum fluorides from the reaction zone. The rate of reduction was about five times more rapid at 900°C than at 1125°C owing to the evolution of the highly volatile aluminum monofluoride at 900°C. At temperatures of 1000°C and above, the gaseous product was aluminum trifluoride, indicating that aluminum monofluoride disproportionates at the higher temperatures. In experiments using 60-g plutonium charges, the plutonium yields in the alloy averaged 98 per cent.

Plutonium-aluminum alloy ingots containing 30 g of plutonium have been prepared by the reduction of plutonium dioxide with aluminum in the presence of cryolite at 1200°C. Powered plutonium dioxide and cryolite in a weight ratio of 1:4 was heated with an aluminum ingot at 1200°C for 15 min. The reduction proceeded rapidly owing to dissolution of the aluminum oxide product in the molten cryolite. Plutonium-reduction yields averaged over 99 per cent.

Beryllium-base alloys have been prepared by reduction in vacuum of both plutonium trifluoride and dioxide. The plutonium trifluoride-beryllium reaction was complete after 25 min at 1125°C and produced a fluoride-free alloy in high yield. Plutonium-beryllium alloys of atom ratios of 1:10 to 1:300 were prepared by evaporating beryllium at 1200°C from a beryllium-rich alloy.

The reduction of plutonium dioxide with beryllium proceeds rapidly at 850°C, even when no flux is present to dissolve the beryllium oxide product. Cryolite, which dissolves up to 7 per cent beryllium oxide, may be used as a flux.

Experiments have also been carried out on the preparation of plutonium alloys of silicon, gallium, thorium, and uranium by the direct reduction of plutonium trifluoride or tetrafluoride.

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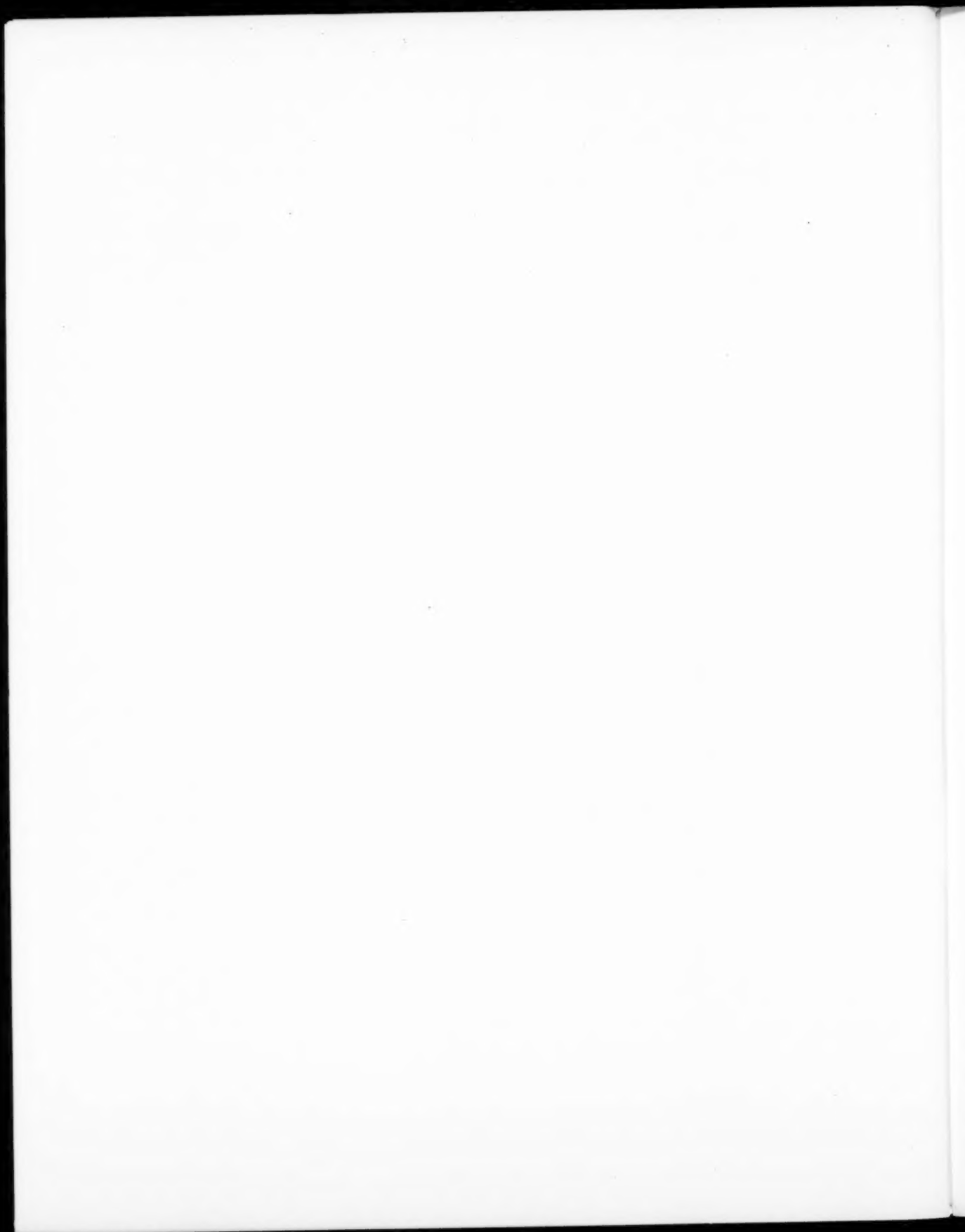
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